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Adsorption Kinetics and Electrode Processes.

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ADSORPTION KINETICS AND ELECTRODE PROCESSES

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The kinetics of adsorption on electrodes is studied for substances which are not reduced or oxidized at the electrode. Adsorption rates are derived for the plane electrode with control by semi-infinite linear diffusion, the streaming mercury electrode, and electrodes in stirred solution. Adsorption at the dropping mercury electrode is also considered briefly. To simplify the treatment it is assumed either (a) that the concentration of adsorbate is so low as to allow linearization of the isotherm, or (b) that the concentration of adsorbate is so large as to correspond to full coverage. In the range of concentrations in which the isotherm can be linearized, adsorption with diffusion control is a slow process and the equilibrium surface concentration is reached only after a long time (perhaps 30 min.). This conclusion is verified experimentally by differential capacity measurements for the adsorption of n-hexyl alcohol on a hanging mercury drop in 1 M potassium nitrate. Data are also presented for adsorption on the dropping mercury electrode.

The effect of adsorbed substances on kinetic parameters for electrode reactions and limiting currents is discussed. Two effects of adsorption in over-voltage phenomena; namely, the decrease in effective area resulting from adsorption and

the variations in kinetic parameters can be separated by determination of the electrode coverage from measurements of the double layer differential capacity. Application is made to the system Ti(IV)/Ti(III) in tartaric acid medium in presence of n-amyl alcohol, cyclohexanol, and thymol. The rate constant characterizing the kinetics of the electrode reaction is essentially independent of coverage ($\theta < 0.4$) for the first two substances and decreases markedly for thymol.

The effect of adsorption on limiting currents is studied by polarography, the electrode coverage during drop life being determined from differential capacity measurements. Variations in limiting current with coverage at the end of drop life are studied for several systems, and it is shown that the decrease in limiting current depends primarily on two factors: the "size" of the reducible species and the structure of the adsorbed film. This conclusion is confirmed by current-time curves during drop life. The interpretation of complete waves complicated by adsorption of foreign substances is discussed, and application to the cadmium wave in the presence of n-hexyl alcohol is made.

Experimental methods are discussed in some detail, and a simple accurate bridge for differential capacity measurements without isolation transformers is described. An extrapolation method for minimization of contamination effects is discussed. It is recommended that the dropping mercury (amalgam) electrode be used in kinetic studies rather than the stationary hanging mercury (amalgam) drop.

CHAPTER I

INTRODUCTION

Three groups of problems arise in the study of the effects of adsorption on electrode processes: (a) influence of adsorption in the absence of electrode reactions; (b) influence of the adsorption of foreign substances (not reduced or oxidized) on the rate of electrode reactions; and (c) influence of adsorption of the reducible and/or reduced species on the characteristics of electrode reactions involving these substances. This investigation will be concerned primarily with the first two problems.

The first group of problems includes two broad studies, namely, the investigation of adsorption equilibria and the kinetics of adsorption. Adsorption equilibria at electrodes were studied by Frumkin (10) and Butler (2) some thirty years ago and recently by Hansen and coworkers (19). It is observed that the surface concentration exhibits a maximum in the neighborhood of the electrocapillary maximum and, in general, approaches zero at sufficiently anodic (displacement by anions) and cathodic (displacement by the solvent, such as water) potentials.

If one excepts recent studies of the kinetics of absorption by electrolysis with superimposed alternating current (4, 13, 31, 32, 42), mass transfer of the adsorbate has generally not been considered, and it has tacitly been assumed that there is no concentration "polarization" of the adsorbate. In other words it is generally assumed that the surface concentration has the equilibrium value corresponding to the concentration of adsorbable substance in the bulk of the solution far from the electrode. This assumption often cannot be made as will be apparent from this work, and a study of adsorption with mass transfer control is of interest. This study is described in Chapter III (a) for control by linear diffusion to a plane electrode, (b) for the dropping mercury electrode, (c) for the streaming electrode, and (d) for stirred solutions. Implications in double layer capacity measurements, electrocapillary curve studies, electrochemical kinetics, and polarography will be discussed.

The second group of problems, namely, the effect of foreign substances on the rate of electrode processes involves two major studies: the effect of adsorption on kinetic parameters for the electrode reaction, and the influence of adsorption under control of the electrode process by mass transfer (effect on limiting currents or transition times). Coverage of the electrode by a foreign substance increases the effective current density and, consequently, the overvoltage. Furthermore, the kinetic parameters for the electrode reaction can also be affected, and

this effect also causes a variation of overvoltage. An extensive search of the literature pertaining to the study of these two effects (9, 11, 12, 33, 34, 36, 37, 47, 48) indicated that they have not been separated.

The influence of adsorption of foreign substances on the distortion of polarographic waves and limiting currents in particular and, to a lesser extent, on transition times has been the object of numerous papers in the polarographic literature (9, 11, 12, 20, 21, 23, 35, 40, 41, 56). Variation of limiting currents with concentration of foreign substance have generally been investigated (9, 12, 41), but no attempt has been made to correlate the effect of adsorption with the electrode coverage. This is not a simple matter, as will be shown, since the electrode coverage varies during the drop life.

Some of the questions raised above are answered, at least partially, in this investigation by the introduction of a novel approach, namely, that the kinetics of adsorption is taken into account and that the electrode coverages are measured. A study is made of the variation of kinetic parameters (Chapter IV) and polarographic limiting currents (Chapter V) with electrode coverage, and the influence of the structure of the adsorbed film is investigated. A method for minimization of the effect of electrode contamination is also described.

CHAPTER II

EXPERIMENTAL METHODS

Three types of measurements were made primarily: (a) determination of double layer differential capacities for the calculation of electrode coverages, (b) impedance measurements for the determination of kinetic parameters for electrode processes, and (c) recording of polarographic current-potential and current-time curves. The first two types of measurements were made with a stationary hanging mercury (amalgam) drop and a dropping mercury (amalgam) electrode. All recordings of current-potential and current-time curves were made with a dropping mercury electrode.

CELL, INSTRUMENTATION, AND PROCEDURE FOR DIFFERENTIAL CAPACITY MEASUREMENTS WITH THE HANGING MERCURY DROP.

A hanging mercury drop similar to that developed by Gerischer was utilized (3, 15). Mercury drops were collected in a glass spoon and then, by rotation of the spoon, hung on a fine gold-plated platinum wire[1] sealed in a drawn-out glass tube.

[1] Instead of hanging the drop on a gold-plated platinum wire, one can use a mercury plated platinum wire and thus prevent contamination of mercury by gold (51).

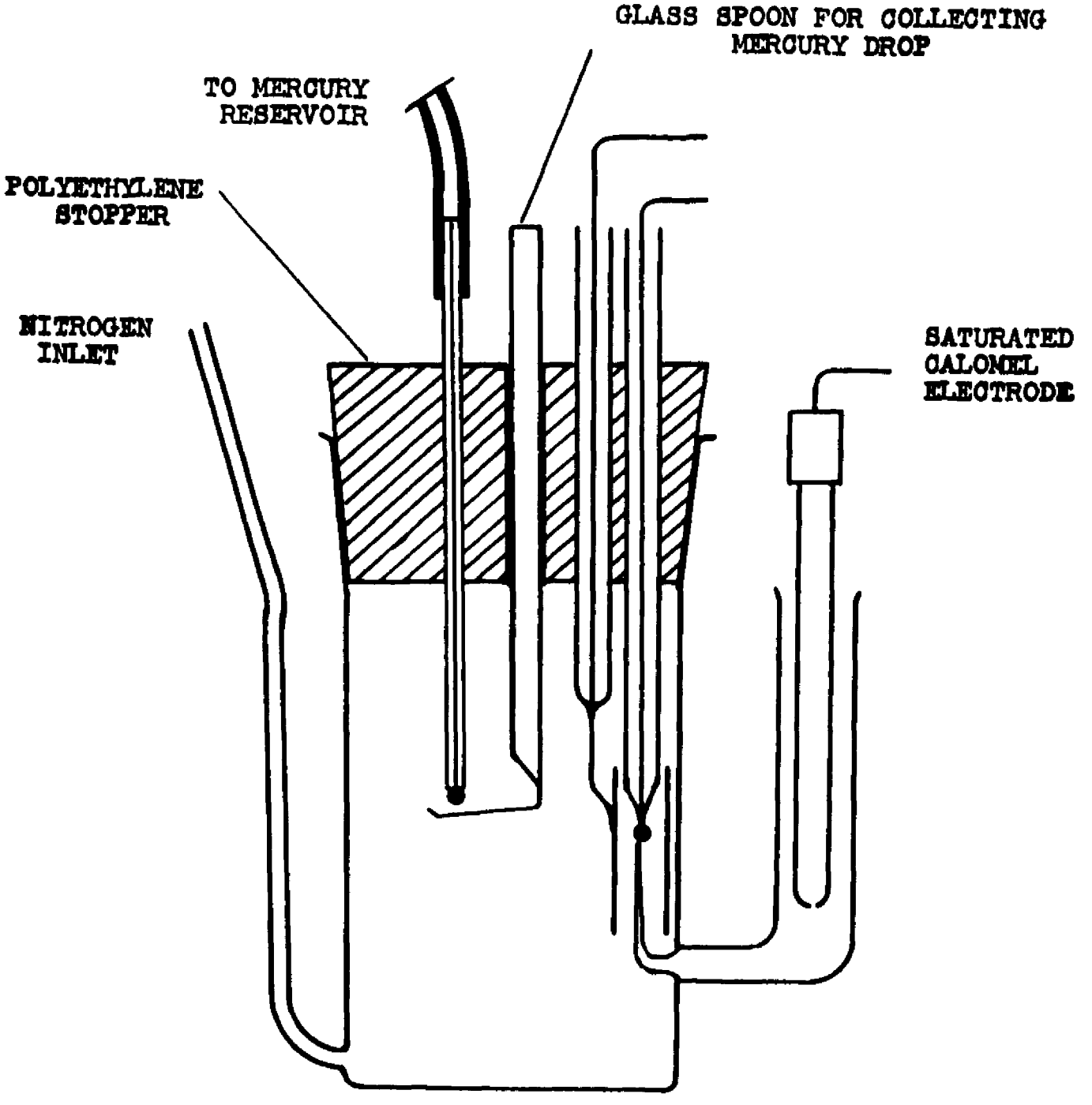

Fig. 1- Cell with Hanging Mercury Drop for Differential Capacity Measurements

This method proved more practical than the one used by Gerischer. The tip of the glass tube was drawn out to avoid shielding of the mercury drop and the resulting dispersion of differential capacity with frequency. The cell was quite similar to that devised by Grahame (18). The mercury drop was surrounded by a cylinder of platinum foil (diameter, 1 cm; length 1.5 cm) which was connected to the A.C. bridge. The potential of the mercury drop was adjusted against a saturated calomel electrode.

Solutions were freed of oxygen by nitrogen. To avoid evaporation of the substance being adsorbed on the electrode (n-hexyl alcohol), the pure electrolyte was first freed of oxygen, and a small volume (1 ml. in general) of an aqueous solution of n-hexyl alcohol was added afterwards. No nitrogen was passed through the solution after the addition of n-hexyl alcohol.

The procedure was as follows: After preparation of the solution in the cell and proper setting of the potential of the mercury drop electrode (see bridge below), a mercury drop was rapidly hung and the differential capacity was measured within 20-30 sec. The bridge was set approximately at the correct resistance and capacity in advance to speed up measurements. The differential capacity was followed until a steady reading was obtained. This required at least 30 min. with the more dilute solutions of hexyl alcohol.

BRIDGE.

The bridge of Fig. 2 was utilized[2] (16, 47, 54). It is described here because it is simpler than bridges with isolation transformers (in the input and detector circuits) often utilized in differential capacity measurements (18).

Components were as follows: R_1 and R_2, matched 100 ohm resistances; R_3 and R_4, 1 megohm; R_5, 0-999.9 ohms decade box; R_6, 0-1 megohm variable resistance; C_1, 0.5 microfarad; C_2 and C_3, 0.05 microfarad; C_4, 0-11 microfarad decade box in 0.001 microfarad steps; C_5, 0-500 micromicrofarads, adjustable; H, 32 millihenry inductance; POT, Leeds and Northrup student potentiometer; OSC, Hulett-Packard oscillator, Model 650A; AMP, Tektronix preamplifier, Model 122; CRO, Dumont oscilloscope, Model 304A; FIL, General Radio filter, Model 1231-P5.

The procedure was as follows: The voltage (peak voltage) applied to the bridge was set approximately at 5 millivolts at 2000 cps; the earth compensation was first adjusted with R_6 and C_5 to achieve balance, switch S being open; the potential of the mercury drop was set with potentiometer POT, and S was closed; the bridge then was adjusted with R_5 and C_4. In general, results were precise within 0.1 per cent.

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[2]We are indebted to Dr. W. Vielstich, formerly a Research Associate in this Laboratory, for having suggested the use of this simple bridge.

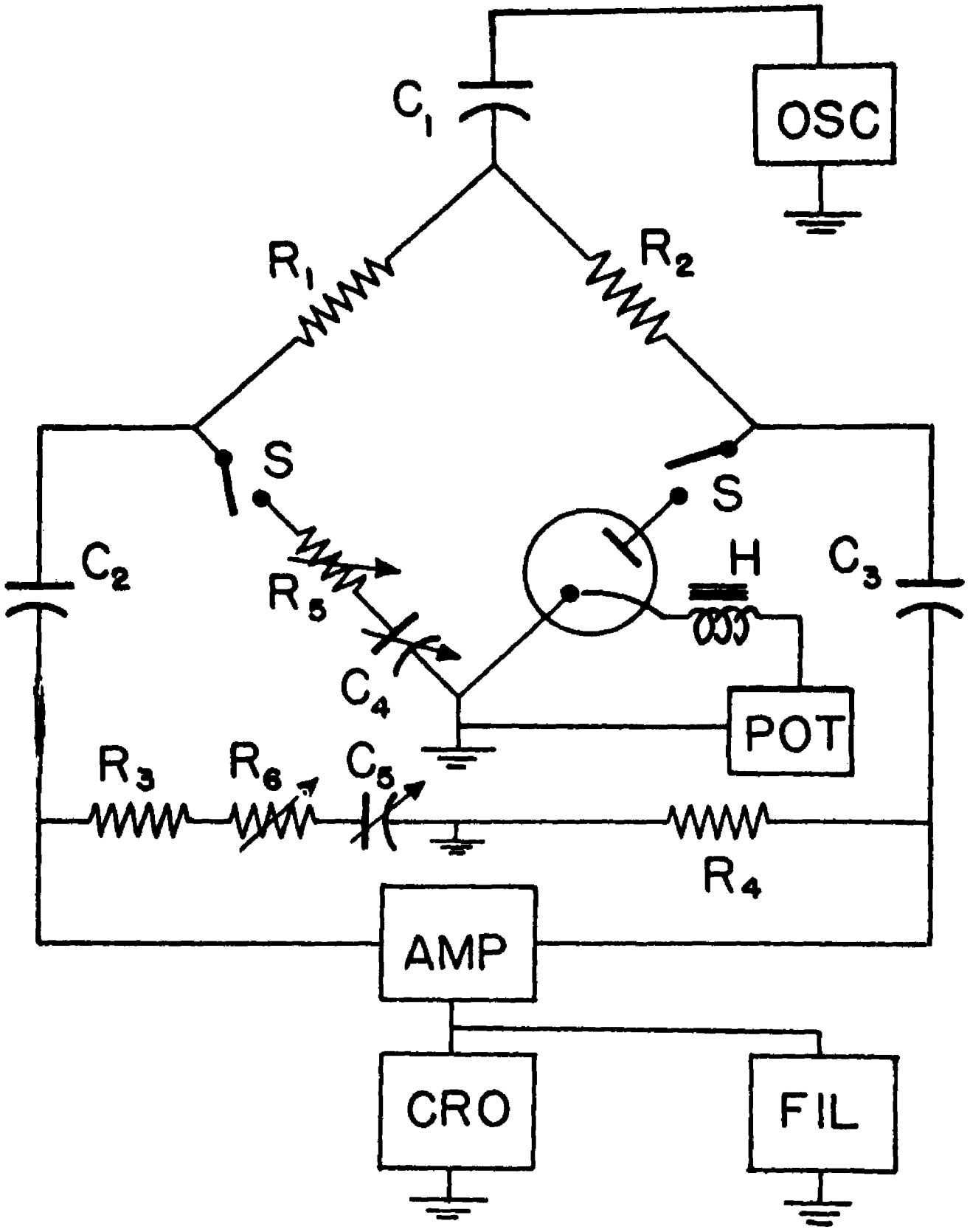

Fig. 2. Bridge for differential capacity measurements.

ELECTRODE COVERAGE MEASUREMENTS WITH DROPPING MERCURY ELECTRODE.

Electrode coverages were determined (a) from differential capacity measurements with an A.C. bridge in the study of the effect of coverage on the rate constant for the electrode reaction, and (b) by direct measurements of the double layer capacity current. The technique for bridge measurements was the same as in the hanging mercury drop cases except that a dropping mercury electrode was used. The bridge was balanced at the end of the drop life.

Capacity current measurements were made with apparatus similar to one used in A.C. polarography (7). The alternating voltage having an amplitude of 0.020 volt was supplied by a General Radio isolation transformer (model 578-B) connected to a Hewlett-Packard oscillator (model 650A) which operated at 35 c.p.s. This low frequency was selected so that the current through the cell was determined, for all practical purposes, by the impedance of the double layer capacity and not by the resistance of the other elements in series with the cell. For this reason, a 47 ohm resistor of the radio type was connected across the output terminals of the secondary of the isolation transformer. The current, as measured by the ohmic drop across a 75 ohm resistor in series with the cell, was recorded with a Tektonix cathode-ray oscilloscope model 535 with preamplifier 53E (sensitivity of 50 microvolts per cm.). The potential of the dropping mercury electrode was adjusted against a saturated calomel electrode by means of a 100 ohm "Helipot" potentiometer.

The latter was calibrated with a Leeds and Northrup student potentiometer.

DETERMINATION OF EXCHANGE CURRENTS AND RATE CONSTANTS FOR ELECTRODE REACTIONS.

Exchange currents were measured by electrolysis with superimposed alternating current. This method is now classical and its theory and methodology need not be discussed in detail here (see 7, 14, 15, 45, 47). Measurements were carried out with the bridge and cell described above. The cell impedance was balanced at the end of drop life against a resistance R_s and capacity C_s in series. The resistance R_e of the supporting electrolyte was measured in a separate experiment. The parallel combination of a resistance R_p and capacity C_p that is equivalent to $R_s - R_e$ and C_s was determined from the equation (C_p is not needed),

$$P_P = (R_S - R_e)\left[1 + \frac{1}{w^2(R_S - R_e)^2 C_S^2}\right] \quad (2\text{-}1)$$

and linear plots of R_p against $w^{-\frac{1}{2}}$ ($w = 2\pi f$, f being the frequency of measurement) were prepared. The exchange current was computed from the extrapolated value of R_p at $w^{-\frac{1}{2}} = 0$: $R_p = RT/nFAi_o$, where R is the gas constant, T is the absolute temperature, n the number of electron involved in the electrode reaction, F the Faraday, and A the electrode area. This method is the same as that applied by Gerischer (14, 15).

The rate constant k_s is readily computed from i_o since $i_o = nFk_sC$, C being the common value of C_O and C_R (see equation

4-1). The transfer coefficient need not be known in the calculation of k_s from i_o when $C_o = C_R$.

POLAROGRAPHIC MEASUREMENTS AND RECORDING OF CURRENT-TIME CURVES.

Current-time curves were recorded by connecting a cathode-ray oscilloscope (Tektronix model 531 with preamplifier 53-54D) to a decade resistance box R in series with the cell. The ohmic drop in R did not exceed a few millivolts. Polarographic measurements followed conventional practice except for deaeration which was carried out by the procedure outlined in the following section. Current-potential curves were recorded with a Sargent polarograph, Model 21. The recorder of this instrument was replaced by a Brown recorder with fast response (1 sec. for full scale deflection).

SOLUTIONS AND CADMIUM AMALGAM.

Distilled water and C.P. chemicals (unless otherwise specified) were used in the preparation of all solutions. The organic liquids were purified by distillation. The titianium solutions were prepared from commercial 20% titanium chloride solution (W.H. Curtin and Co.), whose Ti(III) contents were determined by titration with ferric chloride. Ti(IV) solutions were prepared by air oxidation of Ti(III) in tartaric acid medium. To avoid oxidation of Ti(III), the supporting electrolyte solution containing Ti(IV) was placed in the cell and deaerated for at least 30 minutes before addition of a small quantity of a rather concentrated Ti(III) solution. The concentrations of Ti(III) and Ti(IV) were controlled by polarography before each determination.

In experiments in which adsorbed substances were added, the solution was first deaerated in the cell, as mentioned above, and the organic substance then was added in the form of a small volume (perhaps 1 ml.) of a concentrated (often saturated) aqueous solution. In general, nitrogen was not bubbled through the cell after addition of organic material in order to avoid losses by evaporation.

Cadmium amalgam was prepared by electrolysis of a solution containing weighed amounts of cadmium sulfate and mercury (the cathode) in 1 M sulfuric acid. After exhaustion of the cadmium from solution (24 to 48 hours with continuous moderate bubbling of nitrogen), the amalgam was kept in the electrolysis vessel, a small cathodic current (0.005 amp.) flowing continuously through the cell. Hydrogen was evolved at the cathode after the cadmium had been exhausted from solution. The amalgam was transferred and kept under nitrogen in the dropping amalgam electrode. The cadmium concentration in the amalgam was determined by polarography.

CHAPTER III

KINETICS OF ADSORPTION WITH MASS TRANSFER CONTROL

Adsorption processes are of considerable importance in many fields, and it is therefore of interest to develop suitable treatments for the kinetics of adsorption. Such an analysis is made in this dissertation for the cases in which the adsorption process is entirely controlled by the mass transfer process. This simplification is probably permissible in many cases; for instance, it was shown in recent studies of adsorption kinetics by alternating current methods (11, 12, 31, 32, 42) that adsorption of many polar organic substances on a mercury electrode in unstirred solutions is entirely diffusion controlled. Experimental confirmation of the validity of some of the mathematical treatment is also presented.

1. Control by Semi-infinite Linear Diffusion Boundary Value Problem.

Consider the adsorption on a plane electrode with mass transfer by semi-infinite linear diffusion. The surface of the electrode is supposed to be initially uncovered; the modification in the treatment for a partially covered electrode initially is trivial. The surface concentration Γ of the adsorbable substance at time t is obtained by integrating the flux of the

adsorbate from 0 to t, i. e.,

$$\Gamma = \int_0^t D\left(\frac{\partial c}{\partial x}\right)_{x=0} dt \quad , \qquad (3-1)$$

where D is the diffusion coefficient of the adsorbate, C the concentration of this substance, and x the distance from the electrode. If it is assumed, as previously stated, that the adsorption process is so rapid that there is solely diffusion control, the surface concentration, Γ , is related to the volume concentration at the electrode surface, $C_{x=0}$, by the adsorption isotherm. Thus,

$$\Gamma = \frac{\Gamma_m C}{a + C} \quad , \qquad (3-2)$$

where Γ_m is the surface concentration for maximum coverage, and a is a parameter which is characteristic of the isotherm.

The combination of (3-1) and (3-2) yields the boundary condition for which Fick's equation,

$$\left(\frac{\partial C}{\partial t}\right) = D\left(\frac{\partial^2 C}{\partial x^2}\right) \quad , \qquad (3-3)$$

must be solved. Furthermore, one has $C = C^0$ for $x \geq 0$ and $t = 0$; $C \rightarrow C^0$ for $x \rightarrow \infty$ and $t \geq 0$, C^0 being the bulk concentration of the adsorbate.

Solutions are discussed below for the following two cases: (a) the adsorption isotherm can be linearized,[1] i. e.,

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[1] A linearized isotherm was used by Lorenz (30) in a treatment of electrolysis at constant current which involves an adsorbed reducible species.

$$\Gamma = KC \quad , \quad K = \Gamma_m / a \quad , \quad (3-4)$$

and (b) the case in which C^o is so large that $\Gamma \approx \Gamma_m$ even when $C_{x=0} \ll C^o$. The general case is not treated here because of mathematical difficulties. A general solution could be obtained by means of computer calculations and such calculations are being undertaken at the time of this writing by Dr. Hildebrandt at the Oak Ridge Institute for Nuclear Studies. However, the essential ideas can be presented in a simple treatment.

Variations of Concentration for the Linearized Isotherm.

The ratio of concentrations C/C^o is obtained by solving by Laplace transformations Fick's equation (equation 3-3) for the above initial and boundary conditions.

Firstly, one sets $u = C^o - C$. The Laplace transform of equation (3-3) is, in terms of this new function,

$$\frac{\partial^2 \bar{u}(x,s)}{\partial x^2} - \frac{s}{D} \bar{u}(x,s) = 0 \quad , \quad (3-5)$$

where s is the parameter of the transform. The solution of this differential equation is of the form

$$\bar{u} = A \exp\left[-\left(\frac{s}{D}\right)^{1/2} x\right] + B \exp\left[\left(\frac{s}{D}\right)^{1/2} x\right] \quad (3-6)$$

A and B being integration constants and "exp" represents the exponetial. One has B = 0 because $\bar{u}$ must remain finite for $X \to \infty$. The constant A is determined by substituting

equation (3-4) into equation (3-1) and by taking the transform of the resulting expression. The complete solution to equation (3-5) in terms of the transform is

$$\bar{C} = \frac{C^{o} \exp\left[-(S/D)^{1/2} x\right]}{S^{1/2}\left[(D^{1/2}/K) + S^{1/2}\right]} \quad . \quad (3-7)$$

By taking the inverse transform of (3-7) and solving for the ratio C/C^{o} one obtains

$$\frac{C}{C^{o}} = 1 - \exp\left[\frac{x}{K} + \frac{Dt}{K^{2}}\right] \operatorname{erfc}\left[\frac{x}{2D^{1/2}t^{1/2}} + \frac{D^{1/2}t^{1/2}}{K}\right] \quad , \quad (3-8)$$

where "erfc" represents the complement of the error function, $\operatorname{erfc}\alpha = 1 - (2/\pi^{\frac{1}{2}}) \int_{0}^{\alpha} \exp(-z^{2})dz$.

Variations of C/C^{o} with the distance from the electrode are shown in Fig. 3 for different times after the beginning of the adsorption process and for values $D = 0.5 \times 10^{-5}$ cm. sec.$^{-1}$ and $K = 5 \times 10^{-3}$ cm. These values are the order of magnitude of D and K (for actual cases see below). The concentration in the immediate vicinity of the electrode approaches the bulk concentration C^{o} only after a long time (1000 sec. or more), and adsorption equilibrium is slowly attained. The qualitative interpretation is simple: The gradient of concentration of the adsorbate decreases continuously as adsorption proceeds, and the rate of diffusion drops accordingly.

The surface concentration, C_{s}, at time t is readily obtained from equation (3-8) by noting that, according to

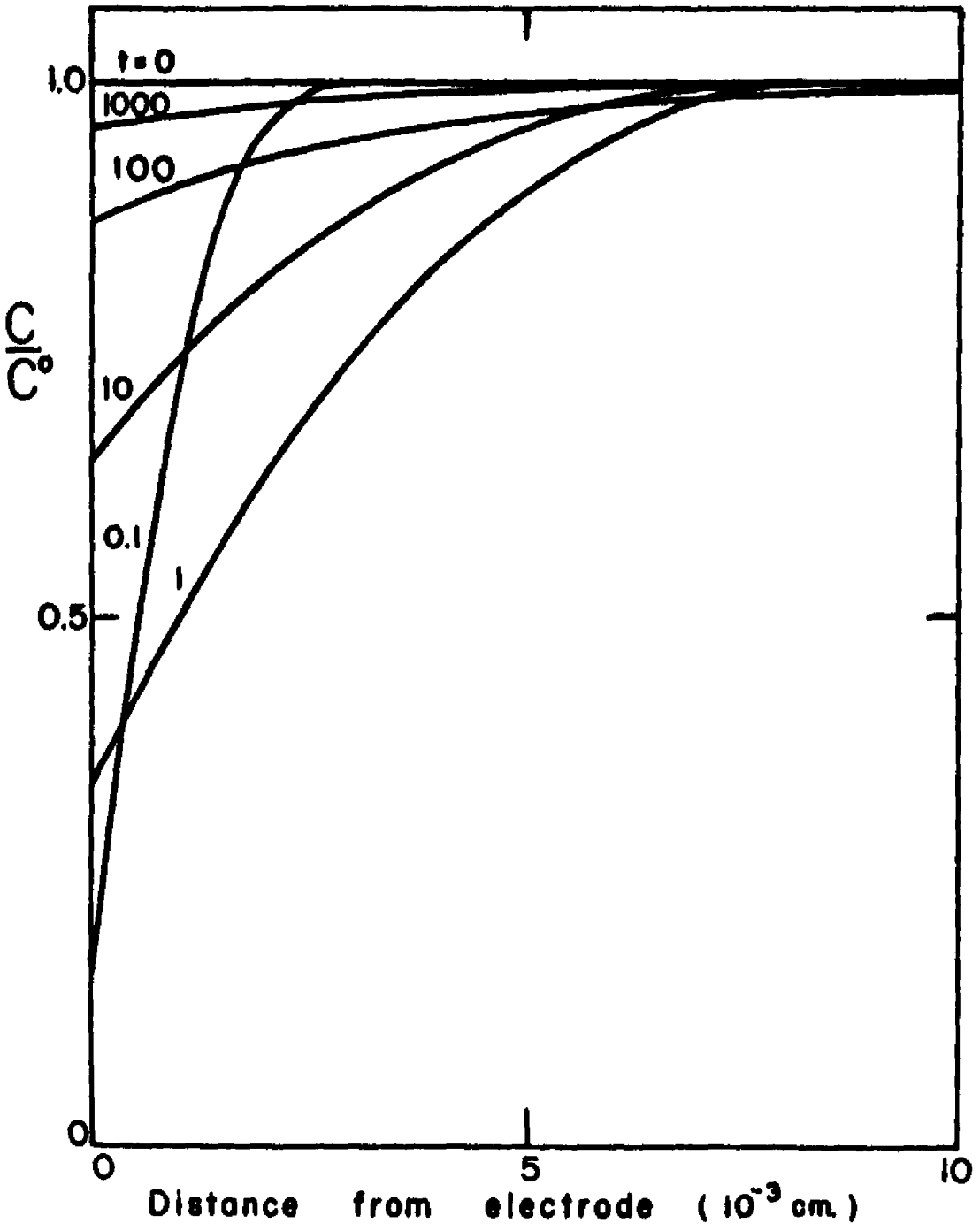

Fig. 3. Variations of C/C^{o} with distance from electrode for different times (in seconds) after the beginning of adsorption and for control by semi-infinite linear diffusion. Data in text.

equation (3-4), $\Gamma_t = KC_{x=0}$. Thus,

$$\frac{\Gamma_t}{\Gamma_e} = 1 - \exp\left(\frac{Dt}{K^2}\right) \operatorname{erfc}\left(\frac{D^{1/2}t^{1/2}}{K}\right), \qquad (3-9)$$

where Γ_e is the equilibrium surface concentration for the bulk concentration C^o, i. e., $\Gamma_e = KC^o$ (equation (3-4). The function in equation (3-9) is tabulated in Carslaw and Jaeger (5). The ratio Γ_t/Γ_e, which is equal to zero at $t = 0$, approaches unity as t tends to infinity. The value of the argument for which there is virtually complete coverage is readily deduced from equation (3-9). For instance, $\Gamma_t/\Gamma_e \geq 0.99$ when $D^{\frac{1}{2}}t^{\frac{1}{2}}/K \geq 56.5$; i. e., for $t > 1.6 \times 10^4$ seconds for the data of Fig. 3. Actually, convection interferes and shortens the time necessary to attain adsorption equilibrium.

The ratio of Γ_t/Γ_e given by equation (3-9) is independent of the bulk concentration of the adsorbable substance because the adsorption isotherm has been linearized in this treatment. Thus, the rate of diffusion is doubled when C^o is changed to $2\,C^o$, but Γ_t/Γ_e is also doubled and, consequently, Γ_t/Γ_e is independent of C^o. Actually, one would find that the time required to reach a given value of Γ_t/Γ_e decreases as C^o increases if the complete adsorption isotherm (equation 3-2) were used.

Variations of Concentrations for the Case in which $\Gamma \approx \Gamma_\infty$ even for $C_{x=0} \ll C^o$.

This case can readily be treated by the Ilkovic equation (44) as written for the case of semi-infinite linear diffusion. It is assumed that the rate of diffusion is the same as for a

process in which $C_{x=0} = 0$ for $t > 0$ and $C_{x=0} = C^o$ for $t = 0$. This major simplification is justified when the bulk concentration of the adsorbate, C^o, is so large that the maximum coverage, Γ_m, is reached even when the volume concentration of the adsorbate at the electrode surface is much smaller than C^o. One then has, in terms of unit area (27, 28),

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{C^o}{(\pi D t)^{1/2}} \quad , \qquad (3-10)$$

By substituting the value from (3-10) for the partial derivative in equation (3-1) and integrating, one obtains

$$\Gamma_t = \frac{2 D^{1/2} C^o}{\pi^{1/2}} t^{1/2} \quad . \qquad (3-11)$$

Equation (3-11) is valid only for values of t for which $\Gamma_t \leq \Gamma_m$. The time τ at which $\Gamma_t = \Gamma_m$ is readily computed from (3-11). Actually, the value Γ_m is approached asymptotically and τ should be infinite; however, because of the very approximate nature of this particular derivation, a finite value of τ is obtained. It is interesting to note that τ is inversely proportional to the square of the bulk concentration C^o.

Experimental Verification.

The differential capacity of an electrode is markedly changed by the adsorption of polar organic substances. The double layer can be represented by an equivalent circuit composed of two capacities in parallel: one capacity for the covered fraction of the electrode, and the other capacity for the

uncovered fraction. On the basis of this model one can write

$$c = c_{\theta=1} + (c_{\theta=0} - c_{\theta=1})(1-\theta) \quad , \qquad (3-12)$$

θ being the electrode coverage. Equation (3-12) holds for the range of potentials in which $c_{\theta=0} > c_{\theta=1}$. At time t, one has $\theta = \Gamma_t/\Gamma_m$, Γ_m being the maximum surface concentration of adsorbate. Likewise, $\theta = \Gamma_e/\Gamma_m$ for $t \longrightarrow \infty$. Hence,

$$\frac{\Gamma_t}{\Gamma_e} = \frac{c_{\theta=0} - c_t}{c_{\theta=0} - c_{t\to\infty}} \quad . \qquad (3-13)$$

Relationship (3-13) was applied to the adsorption of n-hexyl alcohol on a mercury hanging drop in 1 M potassium nitrate. Differential capacities were measured with an A.C. bridge (see Experimental). Values of $c_{t\to\infty}$ measured at -0.700 volt (versus S.C.E.) are shown in Fig. 4. These values were reached after 30 to 60 minutes. The curve and the asymptote were traced to fit a Langmuir isotherm ($\Gamma_m = 8 \times 10^{-10}$ moles-cm.$^{-2}$, $a = 2 \times 10^{-8}$ moles-cm.$^{-3}$, see equation (3-2). The capacity c_t was followed during adsorption, and the corresponding values of Γ_t/Γ_e (Fig. 5) were computed from (3-13).

The theoretical curve deduced from (3-9) is also traced in Fig. 5 for the value $D^{\frac{1}{2}}/K = 0.05$ sec.$^{-\frac{1}{2}}$, i. e., for $K = 4 \times 10^{-2}$ cm. with $D = 0.4 \times 10^{-5}$ cm.^{2} sec.$^{-1}$. This value of K corresponds to $\Gamma = \Gamma_m$ for $C = 2 \times 10^{-8}$ moles-cm.$^{-3}$ for the linearized isotherm (Fig. 4). The value $\Gamma_m = 8 \times 10^{-10}$ moles-cm.$^{-2}$, used in the calculation of K was computed from

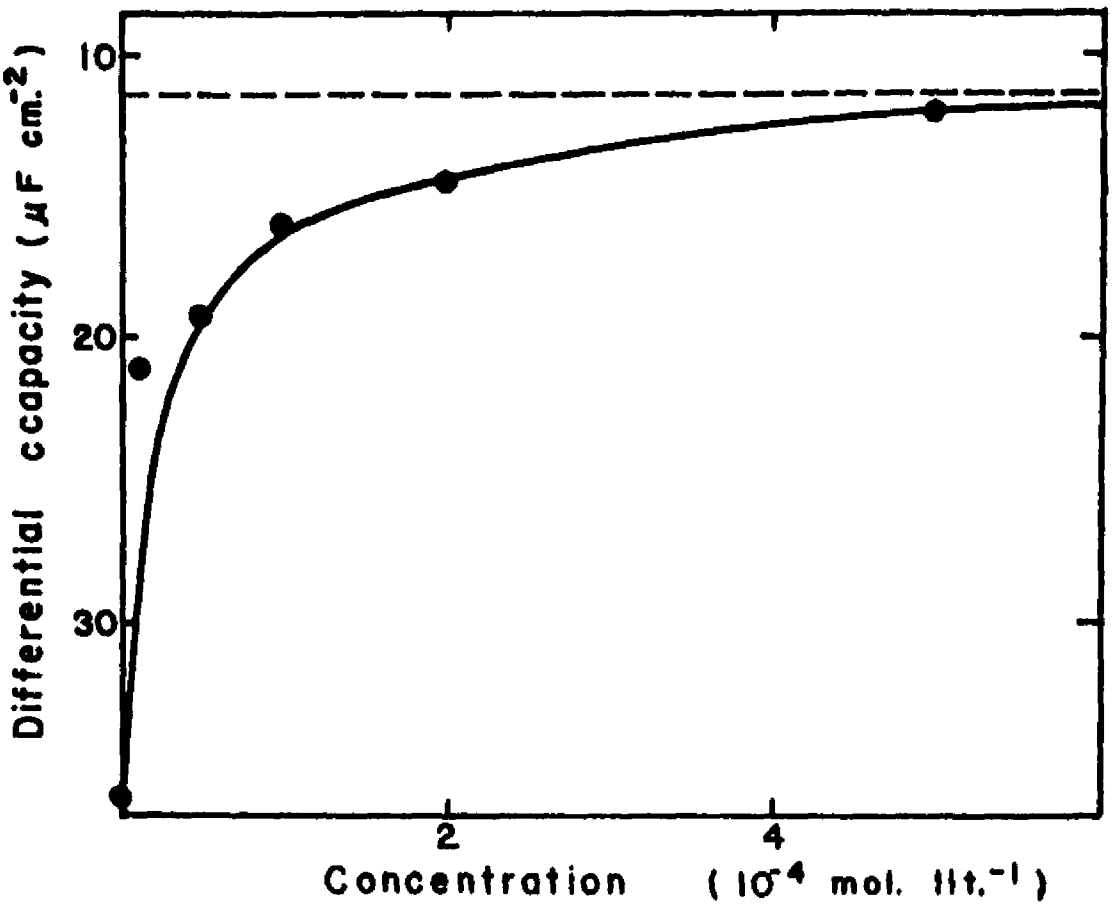

Fig. 4. Differential capacity of hanging mercury drop in 1 M potassium nitrate with varying amounts of n-hexyl alcohol. Capacities measured at -0.700 volt (vs. S.C.E.) and 25° C.

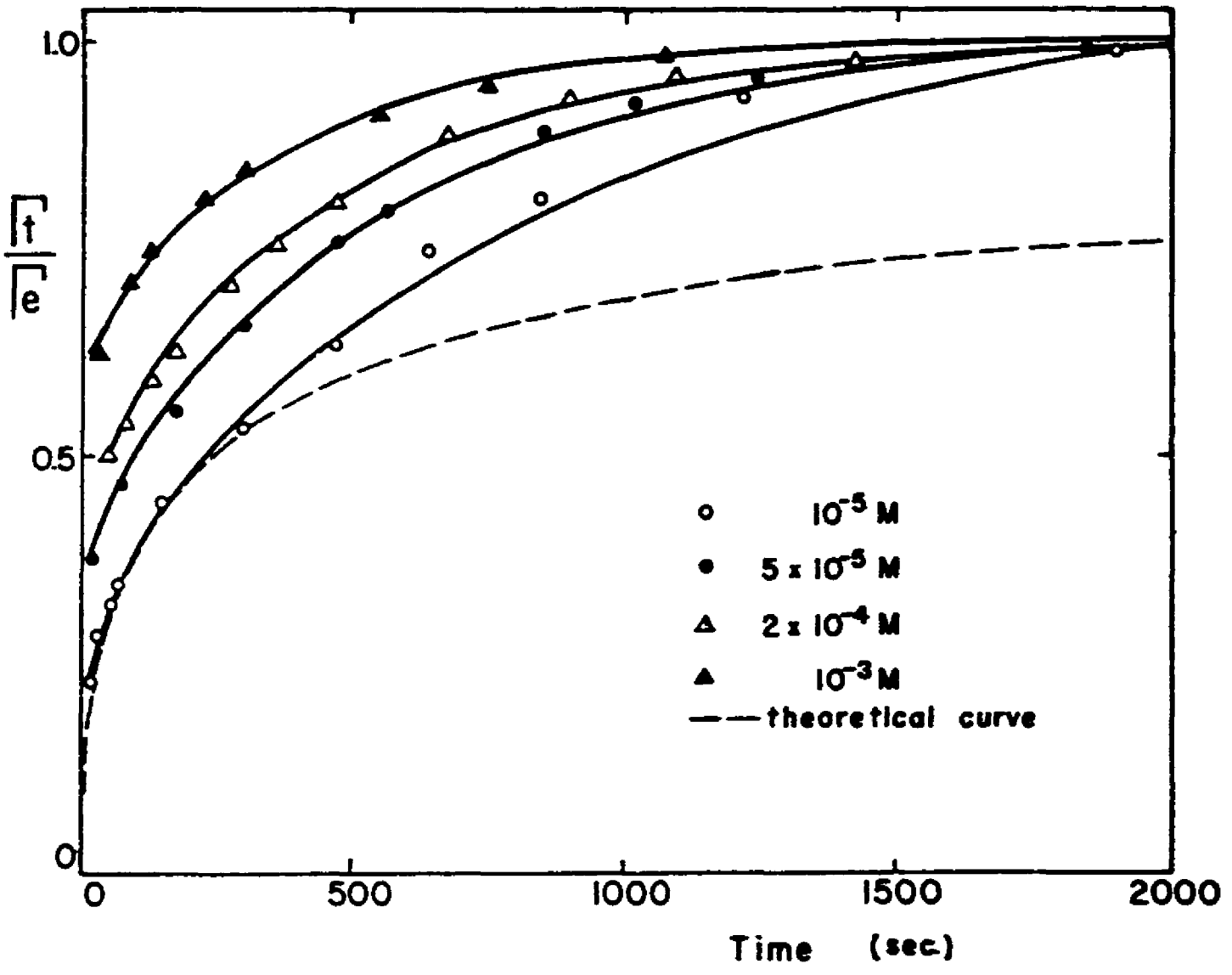

Fig. 5. Variations of Γ_t/Γ_e with time for the conditions of Fig. 4. For theoretical curve $D^2/K = .05$ cm. sec.$^{-\frac{1}{2}}$.

the coverage of 21 x 10^{-16} cm.^{2} per mole quoted by Adam (1) for the adsorption of an aliphatic alcohol with no compression of the film.

The marked departure from theory above 200 seconds in Fig. 5 is to be expected since the theoretical curve corresponds to linear diffusion whereas the experimental results were obtained with a spherical electrode. The disagreement is in the right direction since the rate of diffusion for a spherical electrode is higher than for a plane electrode, all other conditions being the same. Convection also increased the rate of mass transfer of n-hexyl alcohol. Similar experiments were made with a mercury pool electrode, but the results were unreliable, probably because of wetting of the mercury in contact with the wall of the container.

Although this experimental study is only semi-quantitative, it definitely bears out the conclusion that adsorption with diffusion control is a slow process.

Fig. 5 also shows that Γ_2 is reached more rapidly when the bulk concentration of adsorbate is increased, e. g., when the isotherm departs markedly from the linearized form (Fig. 4).

At the time of this writing further experimental verification of equation (3-9) is being attempted by the use of a radiotracer technique. The adsorption of radioactive stearic acid on iron and aluminum is being investigated by Mr. J. Truemper. Preliminary results agree quite well with theory although the preparation of metallic surfaces of reproducible

properties is causing some difficulties, particularly for iron. Results for aluminum appear promising.

2. Control by Diffusion at the Dropping Mercury Electrode

The derivation of the surface concentration at the dropping mercury electrode is the same as above, in principle, but the mathematical treatment is much more involved. Fick's equation (3-3), as modified by Ilkovic for a moving boundary (28),

$$\partial C/\partial t = D\,\partial^2 C/\partial x^2 + (2/3)(x/t)\,\partial C/\partial x , \qquad (3-14)$$

is applied, and equation (3-1) is rewritten in order to take into account the expansion of the drop with time:

$$\Gamma = \tfrac{2}{3} t^{2/3} \int_0^t D\, t^{-2/3} \left(\partial C/\partial x\right)_{x=0} dt . \qquad (3-15)$$

This problem could possibly be solved by computer calculations (and presently these calculations are being attempted) or by making the same transformations that Smuteck (38, 52) used in his elegant treatment of irreversible waves. However, these calculations would be laborious, and only a simple analysis will be presented here.

The rate of diffusion is larger than in the case of linear diffusion because of the expansion of the drop, and Γ/Γ_e approaches unity more rapidly than equation (3-9) predicts for linear diffusion. However, the time required to reach a particular value of Γ/Γ_e should be of the same order of magnitude in both cases. From (3-9) one deduces that $t \propto \Gamma_e^2$ for

$(Dt)^{\frac{1}{2}}/K > 20$, i. e., $D^{\frac{1}{2}}/K > 10$ sec.$^{-\frac{1}{2}}$ for a normal drop time of 4 sec. Since D is of the order of 0.5×10^{-5} cm.^{2} sec.$^{-1}$ in most cases (not for polyelectrolytes), K must be $< 2 \times 10^{-4}$ cm. If one takes the realistic approximate value of $\Gamma_m = 10^{-9}$ moles-cm.$^{-2}$, the above limit of K for the linearized isotherm corresponds to full coverage for $C = 5 \times 10^{-6}$ moles-cm.$^{-3}$. In most cases, $\Gamma \approx \Gamma_m$ for much lower concentrations than 5×10^{-6} moles-cm.$^{-3}$, and K ($\Gamma_m = KC$, see equation 3-4) is appreciably larger than the upper limit of 2×10^{-4} cm. prescribed above. As a result[2], the surface concentration of the adsorbate during drop life is much smaller than the equilibrium value in the range of low concentrations corresponding to the linearized isotherm.

The ratio, Γ_t/Γ_2, at the end of the drop life increases with the bulk concentration of the adsorbate above concentrations corresponding to the linearized isotherm. This can be shown by transposing equation (3-11) to the case of the dropping mercury electrode. The value of $(\partial C/\partial x)_{x=0}$ in (3-10) is multiplied by $(7/3)^{\frac{1}{2}}$ (see Ilkovic equation in polarography (7)), and the result is introduced in equation (3-15). Thus,

$$\Gamma_t = \frac{6}{7}\left(\frac{7}{3}\right)^{1/2} \frac{1}{\pi^{1/2}} C^\circ D^{1/2} t^{1/2}, \qquad (3-16)$$

---

[2]It can be shown from equation (3-9) that $\Gamma_t/\Gamma_2 = 0.10$ for $D^{\frac{1}{2}}/K = 0.05$ sec.$^{-\frac{1}{2}}$ (see experimental verification) and t = 4 sec. This corresponds to the data used in the calculation of the theoretical curve in Fig. 5.

with t such that $\Gamma_t \leq \Gamma_\infty$. From (3-16) one calculates that the time τ at which $\Gamma_t = \Gamma_\infty$ is 0.3 sec. for $D = 0.4 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ and $C^o = 10^{-6}$ moles-cm.$^{-3}$ This calculation which is very approximate corresponds to the most favorable conditions for equilibrium attainment, and the above value of $\tau = 0.3$ is certainly much too low.

Coverage of Mercury Drop During Drop Life.

As previously mentioned, the mathematical treatment of adsorption kinetics with control by diffusion to a dropping mercury electrode is so complex as to require computer calculations. Although such calculations are of interest, it is much simpler to determine the electrode coverage during drop life from variations of the double layer differential capacity.

Capacities could have been measured at different times during the drop life by means of an A.C. bridge with a synchronization device; but the following method, although less accurate, was easier to apply. An A.C. signal of small amplitude (20 millivolts) was applied to a conventional polarographic cell containing the supporting electrolyte and the adsorbed species. The amplitude of the alternating current was recorded during drop life (Fig. 6) under conditions in which the current was proportional to the differential capacity of the double layer (see Chapter II). The scale of current amplitude was readily calibrated in capacitance by substituting a capacitor decade box for the dropping mercury electrode.

The coverage, θ, was calculated (see equations 3-12 and 3-13) by assuming that the differential capacity varies

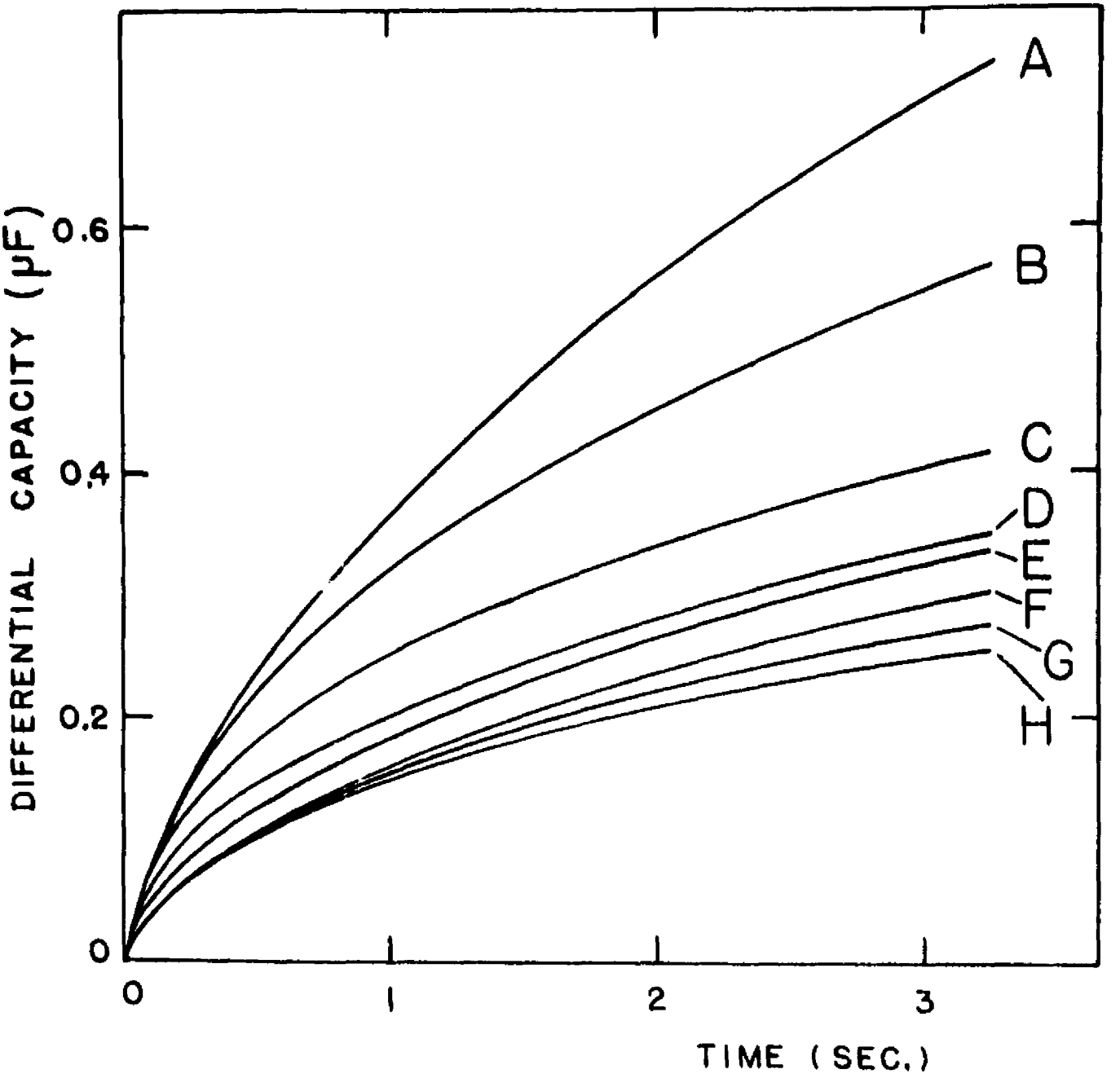

Fig. 6. Variations of differential capacity of mercury drop during drop life at -0.72 volt (vs. S.C.E.) and 30°C. for 0.5 M sodium citrate containing varying amounts of thymol. Concentration of thymol in 10^{-4} M. A(0), B(0.79), C(1.5), D(2.3), E(3.0), F(4.9), G(6.1), H(saturated, i. e., 57). (Curves were obtained from oscillographic traces.)

linearly with θ (Fig. 7). Full coverage was assumed for curve H which was recorded for a saturated solution of thymol (5.7×10^{-3}M). At that concentration, adsorption equilibrium with respect to the bulk concentration is essentially achieved in an early stage of the drop, and the differential capacity at the end of drop life should be independent of drop time (for a constant drop size); this was indeed the case. Since the saturated solution corresponds to the plateau of the adsorption isotherm and the influence of mass transfer is minor, the assumption, $\theta \approx 1$ for curve H is quite valid. Values of θ for $t < 0.5$ sec. were not calculated because of the uncertainty in the reading of Fig. 6. The slight decrease in θ for curve G and F possibly results from the approximate analysis of the data and may not correspond to actual conditions.

3. Control by Diffusion at the Streaming Mercury Electrode

The electrode surface is continuously renewed in the case of the streaming mercury electrode, and it is of interest to determine to what extent the mercury surface is free of adsorbable substance and can be regarded as "clean" in applications to studies of electrochemical kinetics.

The surface concentration will be derived by adaptation of the result for linear diffusion according to a method used by Koryta (24) in his treatment of the limiting current for the streaming mercury electrode. On the basis of the assumptions listed below, Koryta obtained the simplified form of the equation for the limiting current which had been derived more rigorously

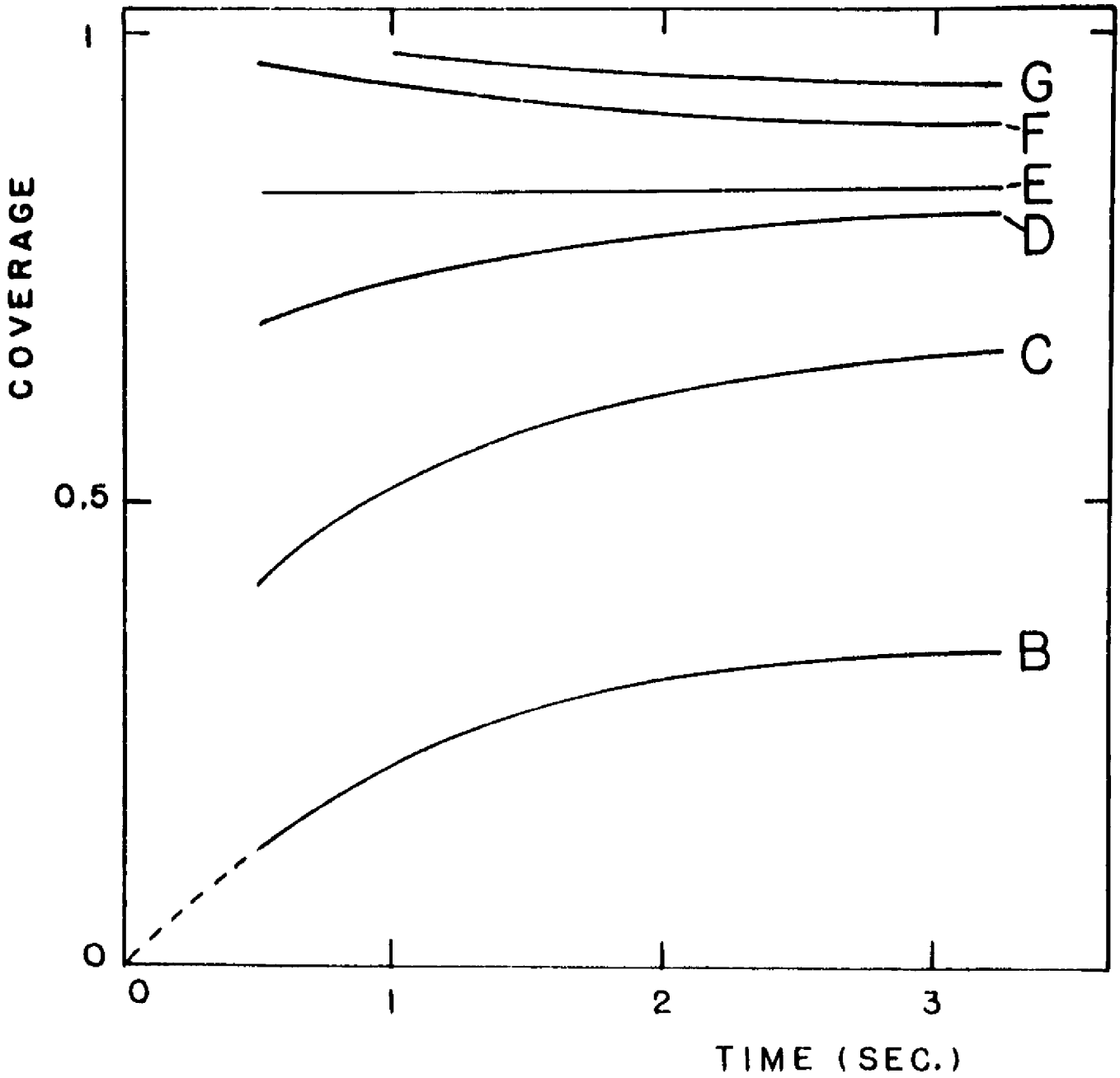

Fig. 7. Surface coverage during drop life for the conditions of Fig. 6.

by Rius and coworkers, and Weaver and Parry (50, 56).

The following assumptions are made: (a) the layer of solution which is adjacent to the mercury column moves at the same velocity as the mercury; (b) this layer is thicker than the diffusion layer; (c) there is virtually no concentration gradient in this layer in the direction parallel to the axis of the mercury stream; (d) diffusion in the layer in the immediate vicinity of the mercury column is treated by Fick's equation for linear diffusion.

The number of moles adsorbed on the electrode is

$$N = \int_0^L D\left(\frac{\partial c}{\partial x}\right)_{x=0} 2\pi r\, dl \,, \qquad (3\text{-}17)$$

where L is the length of the mercury column (supposed to be cylindric), l is the distance from the tip of the capillary to the annular zone of height dl and r is the radius of the mercury stream. The gradient of concentration $\left(\frac{\partial c}{\partial x}\right)_{x=0}$ in equation (3-17) is evaluated from equation (3-8). The latter contain the variable t which is converted to l by noting that t = l/v where v is the velocity (assumed to be uniform) of the mercury stream. Thus, for l = L the following expression is obtained:

$$N = 2\pi r L K C^0 \left\{ 1 - \exp\left(\frac{DL}{K^2 v}\right) \operatorname{erfc}\left[\frac{1}{K}\left(\frac{DL}{v}\right)^{1/2}\right] \right\}. \qquad (3\text{-}18)$$

The value of N_e for adsorption equilibrium is in view of equation (3-4)

$$N_e = 2\pi r L K C^0 . \qquad (3\text{-}19)$$

and

$$\frac{N}{N_e} = 1 - \exp\left(\frac{DL}{K^2 v}\right) \operatorname{erfc}\left[\frac{1}{K}\left(\frac{DL}{v}\right)^{1/2}\right] . \quad (3\text{-}20)$$

The ratio N/N_e has the same form as the ratio Γ_t/Γ_e for linear diffusion (see equation 3-9), and the dimensionless parameter $(1/K)(DL/v)^{\frac{1}{2}}$ simply replaces the argument $(Dt)^{\frac{1}{2}}/K$.

Because of the assumptions underlying equation (3-20), this formula is only approximate, but the order of magnitude of N/N_e can be evaluated from it. For instance, one has $N/N_e = 0.6$ percent for $D^{\frac{1}{2}}/K$ (see experimental verification), $L = 0.5$ cm., and $v = 50$ cm. $sec.^{-1}$; and the electrode is thus virtually free of adsorbate. This could be advantageous in electrochemical kinetics where contamination of electrodes (even mercury or amalgam electrodes) is a serious obstacle to the precise determination of kinetic parameters for electrode processes. However, it must also be pointed out that serious experimental difficulties may be encountered if a streaming mercury electrode is used in kinetic studies. Not only must the excessive requirements for large quantities of mercury be considered, but also the large increase in the capacity current may be sufficient to obscure the faradaic current (i. e., current involved in reduction or oxidation and not in the changing of the double layer) thus making electrochemical kinetic studies considerably more difficult.

The case in which the bulk concentration of adsorbate is so large as to correspond to virtual saturation of the electrode

surface can be analyzed by following the same procedure as for the linear diffusion to the plane electrode. Details will not be given here because the result is of little practical value.

4. Control by Diffusion in Stirred Solutions

The surface concentration of the adsorbate is easily obtained on the basis of the concept of the Nernst diffusion layer thickness. Thus,

$$\left(\partial C/\partial x\right)_{x=0} = \left(C^0 - C_{x=0}\right)/\delta \,, \quad u = C^0 - C \,, \qquad (3\text{-}21)$$

where δ is the thickness of the diffusion layer. By substituting in equation (3-1) the gradient from equation (3-21) u/δ, and differentiating the result with respect to t, there follows the differential equation,

$$\frac{du}{dt} = -\frac{Du}{K\delta} \qquad (3\text{-}22)$$

The solution to the above expression is

$$C = C^0\left[1 - \exp\left(-\frac{Dt}{K\delta}\right)\right] . \qquad (3\text{-}23)$$

One obtains for the linearized isotherm (equation 3-4)

$$\frac{\Gamma_t}{\Gamma_e} = 1 - \exp\left(-\frac{Dt}{K\delta}\right) . \qquad (3\text{-}24)$$

The electrode is rather rapidly covered: $\Gamma_t/\Gamma_e = 0.98$ for t = 120 sec., $D^{\frac{1}{2}}/K = 0.05$ sec.$^{-\frac{1}{2}}$, and $\delta = 0.003$ cm. (an order of magnitude for not too vigorous stirring).

5. Implications

Double Layer Capacity Measurements.

Double layer capacity measurements are somewhat in error when adsorption equilibrium is not attained for adsorbable species. This is the case in the study of the adsorption of polar organic molecules on mercury, when the differential capacity is measured with a dropping mercury electrode and the concentration of the organic substance is low. The correct dependence of the differential capacity on frequency is nevertheless obtained because the diffusion layer is much thicker than the layer in which the concentration of adsorbate varies periodically with time. However, the surface concentration of adsorbate is smaller than the value corresponding to the bulk concentration. It is observed that the characteristic two desorption peaks in the curve differential capacity against potential disappear as the concentration of adsorbate is decreased. When adsorption equilibrium is not attained with the dropping mercury electrode, the peaks should disappear at higher concentrations than for curves obtained with the hanging mercury drop.

Likewise, differential capacities measured with the dropping mercury electrode for low electrolyte concentration (10^{-3} M or less) could be somewhat erroneous when the anion (or cation) is adsorbed. The theoretical analysis made above does not apply to this case because of complications resulting from migration and the structure of the double layer, but the conclusion about the slowness of adsorption is still qualitatively

valid. The same comment can be made for polyelectrolytes (43). Fortunately, most measurements of differential capacity for pure electrolytes are made at concentrations at which adsorption equilibrium is attained.

The value of the parameter $(Dt)^{\frac{1}{2}}/K$ for the system being investigated can serve as a guide in deciding whether adsorption equilibrium is attained. The condition $(Dt)^{\frac{1}{2}}/K \geq 20$ should be fulfilled (see equation 3-9). A simpler test is to change the head of mercury and determine whether the differential capacity per unit area varies with drop time. When equilibrium is not attained, the coverage at the end of the drop life decreases with drop time (see section on Polarography below), and the differential capacity per unit area varies accordingly.

Non-attainment of adsorption equilibrium could be avoided by the use of a stationary mercury electrode, but progressive contamination of the electrode by traces of impurities might be very difficult to avoid. The hanging mercury drop is preferable to the mercury pool[3] because of better reproducibility of area. Another possible solution is the use of the rotating dropping mercury electrode developed for voltammetric studies by Stricks and Kolthoff (53).

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[3]A mercury pool electrode was recently used in differential capacity measurements (19).

Electrocapillary Curves.

The foregoing considerations can be transposed to the "drop weight" method for the determination of electrocapillary curves. Somewhat erroneous results can be expected particularly in studies at low concentration of electrocapillary active substances. Although results are then affected by a systematic error, they can be precise and analytical application is possible.

Electrochemical Kinetics.

Since Chapter IV deals with the effect of adsorption on kinetic parameters for electrode reactions, a discussion of the implications of the foregoing study in electrochemical kinetics will be reserved for this chapter.

Polarography.

The departure from adsorption equilibrium (with respect to the bulk concentration) at the dropping mercury electrode may be relavent in a variety of polarographic studies; maximum suppressors, catalytic waves of alkaloids, distortion of waves, depression of limiting current by adsorption of foreign substances, etc. Application to polarography of some of the ideas developed in this chapter will be given in Chapter V.

CHAPTER IV

EFFECT OF ADSORPTION OF FOREIGN SUBSTANCES ON KINETIC PARAMETERS FOR ELECTRODE PROCESSES

It was pointed out in Chapter I that the adsorption of a foreign substance (not reduced or oxidized) on electrodes causes an increase in overvoltage. Two reasons can be advanced for the variation of overvoltage: (a) a decrease in effective area, and (b) a variation of the kinetic parameters for the electrode reaction. A method for the separation of the effects of these two factors is discussed and applied in this chapter. Minimization of the influence of electrode contamination in kinetic studies will be discussed first.

Reactions for which the reducible species, O, is soluble in solution and the reduced species, R, is soluble either in solution or in mercury (amalgam) will be considered. These electrode reactions can be characterized by their exchange current density (3)

$$i_o = nF k_s C_O^{(1-\alpha)} C_R^{\alpha} \qquad (4-1)$$

provided that they proceed with a single rate determining step involving n electrons. The notations in (4-1) are: F the faraday, k_s the rate constant at the standard potential for the

couple O + ne = R, α the transfer coefficient for the cathodic process, and the C's, the bulk concentrations. The kinetic parameters α and i_o or k_s characterize the electrode reaction.

Minimization of the Effect of Electrode Contamination.

Since adsorption with diffusion control is a slow process at low concentrations of the adsorbate (see Chapter III, section 1), stationary electrodes become progressively contaminated upon exposure to a solution containing traces of adsorbable impurities. This contamination may cause a serious error in the determination of i_o, k_s, and α and it is suggested that these parameters be measured, whenever feasible, with a dropping mercury (or amalgam) electrode rather than with a stationary mercury electrode.

The advantage of the dropping mercury electrode over the hanging mercury drop can be inferred from the recent work of Gerischer and Stauback (17) on the kinetics of the mercurous ion-mercury electrode. These authors observed that exchange currents obtained with a dropping mercury electrode for different concentrations of mercurous ion were about three times larger than the values for the hanging mercury drop. Two different methods, A.C. electrolysis and the potential step method, were applied in these two sets of measurements and this might account for the discrepancy on the exchange current values. However, the lesser contamination of the dropping mercury electrode may well be the explanation of the difference between the two sets of results.

The comparison between the dropping amalgam electrode and the stationary hanging amalgam drop was made for the discharge of Cd^{++} on cadmium amalgam. Values of k_s as obtained by

electrolysis with superimposed alternating current (see Chapter II) are given in Table I. The reaction is quite fast and is almost beyond the range of the A.C. electrolysis ($k_s \lesssim 0.1$ to 1 cm. sec.$^{-1}$ for equipment now available), and consequently measurements were made at 0° rather than at room temperature. Solutions were prepared with distilled water and no impurity was added intentionally. Oxygen was removed by tank nitrogen which probably contained traces of organic impurities (oil that could have been removed by combustion over copper oxide).

The rate constant k_s decreased markedly upon exposure until the limiting value of 0.0038 cm. sec.$^{-1}$ was reached after two hours. Measurements were also made with a dropping amalgam electrode and the approximate (reaction too fast for apparatus) values $k_s \approx 0.2$ cm. sec.$^{-1}$ was obtained for three different drop times (5.34, 3.54, and 2.32 sec.). The value of k_s was independent of drop time at least for the relatively poor accuracy achieved for such a fast process. Note, however, that the k_s obtained with the dropping amalgam electrode is about five times larger than the value obtained with a hanging amalgam electrode after a 20-minute exposure.[1]

The contamination effect is very pronounced for the cadmium electrode because the equilibrium potential (approximately

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[1] At 25°, $k_s \approx 0.6$ cm. sec.$^{-1}$ according to Randles and Somerton (49). The value $k_s \approx 0.04$ cm. sec.$^{-1}$ in 1 M sodium sulfate with a hanging amalgam drop electrode by different investigators (3, 14) is probably too low on account of contamination.

Table I

Values of k_s Obtained with a Hanging Amalgam Drop for the Reaction[a] $Cd^{++} + 2e^- = Cd(Hg)$ at 0°C.

Time exposed to solution in min.	k_s cm. $sec.^{-1}$
20	0.037
40	0.016
50	0.0065
120	0.0038

[a]Solution composition: 6.0×10^{-3} M. Cd^{++}
1.0 M KNO_3

Amalgam composition: 6.0×10^{-6} moles/cc.

-0.6 volt vs. S.C.E.) is near the electrocapillary maximum and, therefore, in the range of maximum adsorption of neutral polar organic impurities. At any rate, it is suggested that a dropping mercury (amalgam) electrode be used in the determination of kinetic parameters for electrode reactions. Stationary electrodes can be used provided that measurements are made within a few seconds of exposure to the solution (the rate of adsorption decreases with time of exposure), but a dropping electrode is probably more practical. It may even be useful to measure i_o, k_s, and α for different drop times and extrapolate the data to time zero. This procedure should be useful in the study of "large" reducible or oxidizable ions and molecules for which the contamination effects are very pronounced (see Chapter V). Extrapolation of kinetic data against the square root of drop time is suggested because the electrode coverage for low concentrations and short times is approximately proportional[2] to $t^{\frac{1}{2}}$. This method, however, is not rigorous because the measured values of i_o, k_s, and α are not necessarily linear functions

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[2]For arguments much smaller than unity, one can write equation (3-9) in the form

$$\theta \approx \frac{2 D^{\frac{1}{2}} t^{\frac{1}{2}}}{\pi^{\frac{1}{2}} \gamma}$$

by noting that the exponetial is then practically equal to unity and that the error function can be expanded in series, only the first two terms being retained.

of the electrode coverage. Furthermore, this extrapolation is based on an equation which is rigorous for the plane electrode but only approximate to the dropping mercury electrode.

Electrode Coverage and Variation of the Rate Constant k_s.

The effect of electrode coverage by a foreign substance on k_s was studied for the reaction Ti(IV) + e = Ti(III) on mercury in tartaric acid. This electrode reaction was selected because k_s (9.0×10^{-3} cm. $sec.^{-1}$), as first measured by Randles and Somerton (48), is well within the range of application of A.C. electrolysis. Furthermore, the formal potential (-0.42 volt vs. S.C.E.) is in the neighborhood of the electrocapillary maximum; i. e., in the range of maximum adsorption of polar organic substances.

The effect of three substances was studied: cyclohexanol, n-amyl alcohol, and thymol. Electrode coverages (Table II) were determined from measurements of the differential capacity of the double layer in the absence of Ti(IV) and Ti(III) as previously described (see Chapter III). All measurements including those for k_s were made at the end of drop life just before the drop was dislodged from the capillary (see Chapter II).

Variations of the rate constant k_s of equation (4-1) with coverage, θ, are shown in Fig. 8. Values of k_s were calculated for the effective uncovered area; consequently, errors on θ are reflected on k_s. Data for amyl alcohol were less reproducible than for cyclohexanol and thymol. Values of k_s at $\theta = 0$ are the constants measured at the end of drop life (lower points) and the

Table II

Electrode Coverage versus Concentration of Adsorbate for Adsorption on Mercury at 30°C. and -0.41 Volts (vs. S.C.E.) in 1.0 M Tartaric Acid and 0.1 M Sodium Chloride[a]

Cyclohexanol		n-Amyl Alcohol		Thymol	
C mM	θ	C mM	θ	C mM	θ
0.5	0.10	0.1	0.11	0.04	0.17
1.0	.13	.2	.12	.08	.21
1.5	.15	.3	.12	.12	.26
1.9	.17	1.3	.29	.15	.30
2.4	.18	2.3	.42	.19	.36
3.3	.21				
4.5	.26				

[a]Capillary characteristics: $m = 2.70$ mg. $sec.^{-1}$, $t = 3.5$ sec.

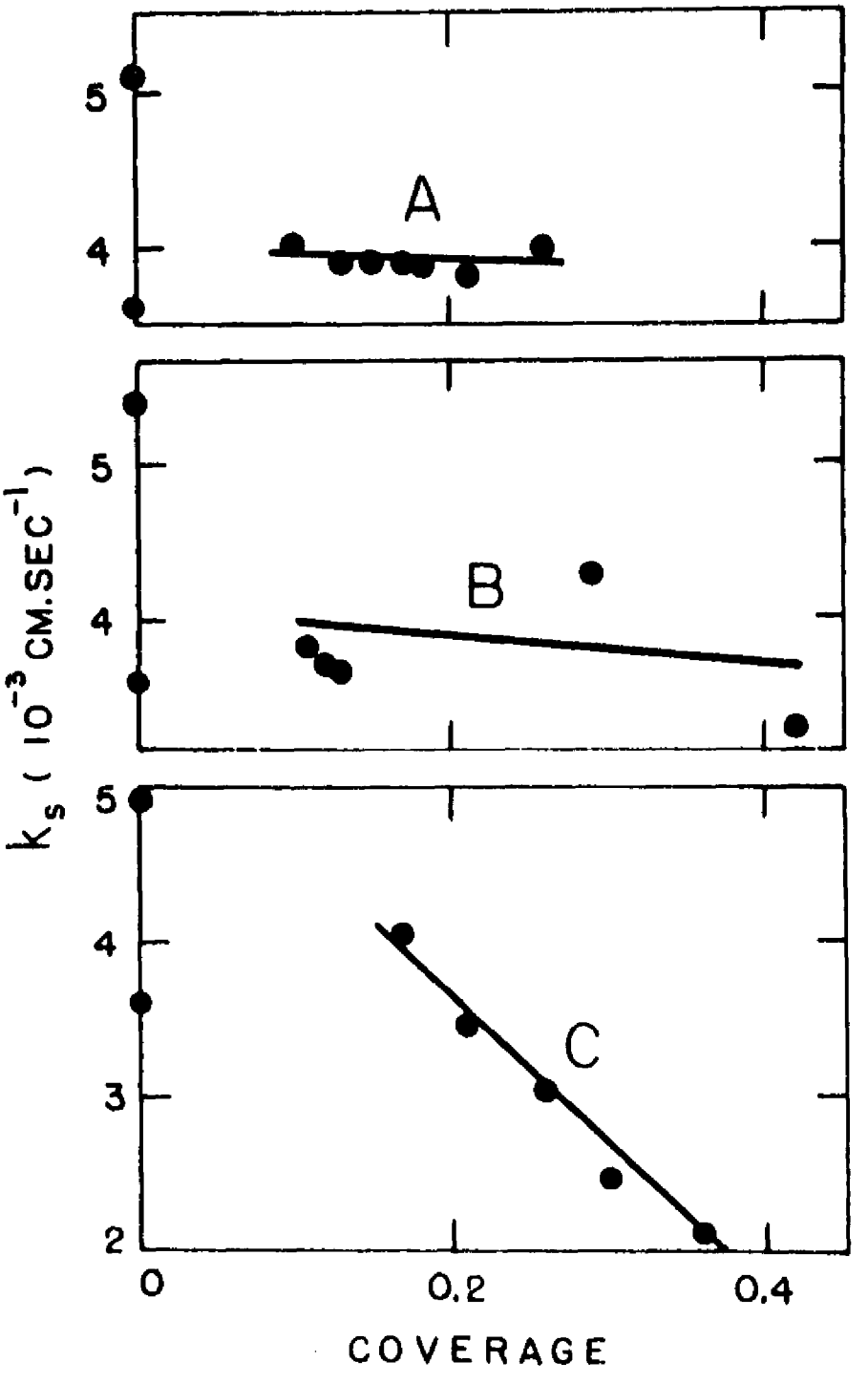

Fig. 8. Variation of k_s of equation (4-1) with electrode coverage for the reaction Ti(IV) + e = Ti(III) in a solution 6 x 10^{-3} M Ti(IV), 6 x 10^{-3} M Ti(III), 1 M tartaric acid, and 0.1 M sodium chloride (A) cyclohexanol, (B) n-amyl alcohol, and (c) thymol.

values extrapolated to t = 0. The points obtained by the former method are too low because no correction was made for the partial coverage of the electrode by impurities. The extrapolated values of k_s are too high because of the pronounced decrease of k_s with increasing drop time (see below). Values of k_s for $0 < \theta < 0.1$ were not obtained because of electrode contamination (probably by traces of oil in the nitrogen). Evidence of contamination without addition of organic substance was provided by the variation of differential capacity of the electrode in the supporting electrolyte when the drop time was varied (the drop size was essentially constant): 0.73, 0.76, 0.77, and 0.80 microfareds for drop times of 6.64, 3.50, 2.54, and 0 (extrapolated value) sec., respectively.

If the range $\theta = 0$ to 0.1 is excluded because the interpretation is uncertain on account of contamination, one concludes from Fig. 8 that in the case of cyclohexanol and n-amyl alcohol the increase in overvoltage is primarily due to the decrease in effective area rather than a variation of k_s.[3] In the case of thymol, the decrease in k_s is also very significant. It is thus possible by coupling kinetic data determinations with electrode coverage measurements (by differential capacity studies or other methods such as surface tension measurements) to separate

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[3]It should be remembered that a decrease of the transfer coefficient would also affect the overvoltage.

the effect of electrode coverage from the variations of the parameter k_s.

A similar study was undertaken to determine the variations of the transfer coefficient α (equation 4-1) with electrode coverage, but an unexpected difficulty arose; it was observed that k_s, as measured for a constant ratio of Ti(IV)/Ti(III), varied with the total titanium concentration. Data were as follows: k_s = 7.2, 4.9, and 4.1 x 10^{-3} cm. $sec.^{-1}$ for total concentrations of titanium of 6, 12, and 26 mM, respectively, the ratio Ti(IV)/Ti(III) being equal to 1 in all cases (values of k_s extrapolated to t = 0 during drop life). It was not possible under these conditions to determine α from the variation of the exchange current with the concentration of one reactant, the concentration of the other reactant being kept constant.[4] This variation of i_o could be due to a variation of the relative concentrations of several complexes or to a purely chemical step proceeding electron transfer. It could also be caused by preferential adsorption of one of the titanium ions involved in the electrode reaction (29). Some evidence in favor of the latter explanation is the variation of the measured k_s with drop time. It was observed that k_s decreased by approximately 50 per cent when the drop time varied from 2 to 8 seconds.

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[4] A plot of log i_o against the logarithm of the varying concentration is a straight line whose slope yields α (equation 4-1) (3, 14).

The adsorption of the reducible and/or the reduced species may alter the values of θ in Fig. 8 since the latter data were deduced from measurements with the supporting electrolyte alone. It is believed that the resulting error, if any, is not serious because the electrode potential was within 0.1 volt from the electrocapillary maximum, i. e., in a range in which displacement of organic substances by ion adsorption is not very pronounced.

CHAPTER V

EFFECT OF ADSORPTION ON CURRENT-POTENTIAL CURVES AND LIMITING CURRENTS

Method of Study.

The "blocking" of an electrode by an adsorbed organic substance in the range of the limiting current can be regarded as a heterogenous process preceding the electrochemical reaction. According to this simplified model, the reducible species must penetrate the film before reduction can take place. One can postulate that the rate of penetration is a first order process and thus introduce rate constants for penetration and its reverse process. These parameters which would characterize the penetration process could be measured, in principle, by methods of non-steady state electrolysis (potential-step and current-step methods). Unfortunately, such measurements appear difficult because the surface coverage for given conditions varies with potential (2, 10), and application of non-steady state electrolysis would require a variation of potential of several tenths of a volt from the potential at which there is virtually no reduction to the range corresponding to the limiting current or transition time. Likewise, polarography cannot easily be applied because the electrode coverage varies continuously during the drop life, and the resulting mathematical analysis

would be very complex. While these difficulties could be overcome in some cases, it is more fruitful to adopt a simpler approach, namely, to measure limiting currents in polarography for known coverages of the mercury drop. Interesting results on the effect of the adsorbed species and the nature of the reducible substance can be obtained as will be shown.

Electrode Coverage and Limiting Currents.

The addition of an adsorbed substance (not reduced or oxidized) affects polarographic waves in two ways: (a) waves become more irreversible because of an increase in overvoltage, and (b) the limiting current may decrease because of the partial coverage of the dropping mercury electrode. The magnitude of these effects vary greatly from one system to another. For instance, the wave may remain essentially "reversible" (it obeys the Nernst equation) up to appreciable coverage when the exchange current of equation (4-1) is large enough (8). Likewise, the effect of blocking is hardly noticeable in some cases; whereas in other instances the limiting current may drop to a very small fraction of its value in the absence of adsorbed substance.

Examples of current-potential curves obtained with varying amounts of quinoline are shown in Fig. 9 for the reduction of Cu(II) in 0.5 M sodium citrate. Maximum currents during drop life are plotted. The range of markedly cathodic potentials at which quinoline should be desorbed could not be explored because of the reduction of this substance (22). However, by changing

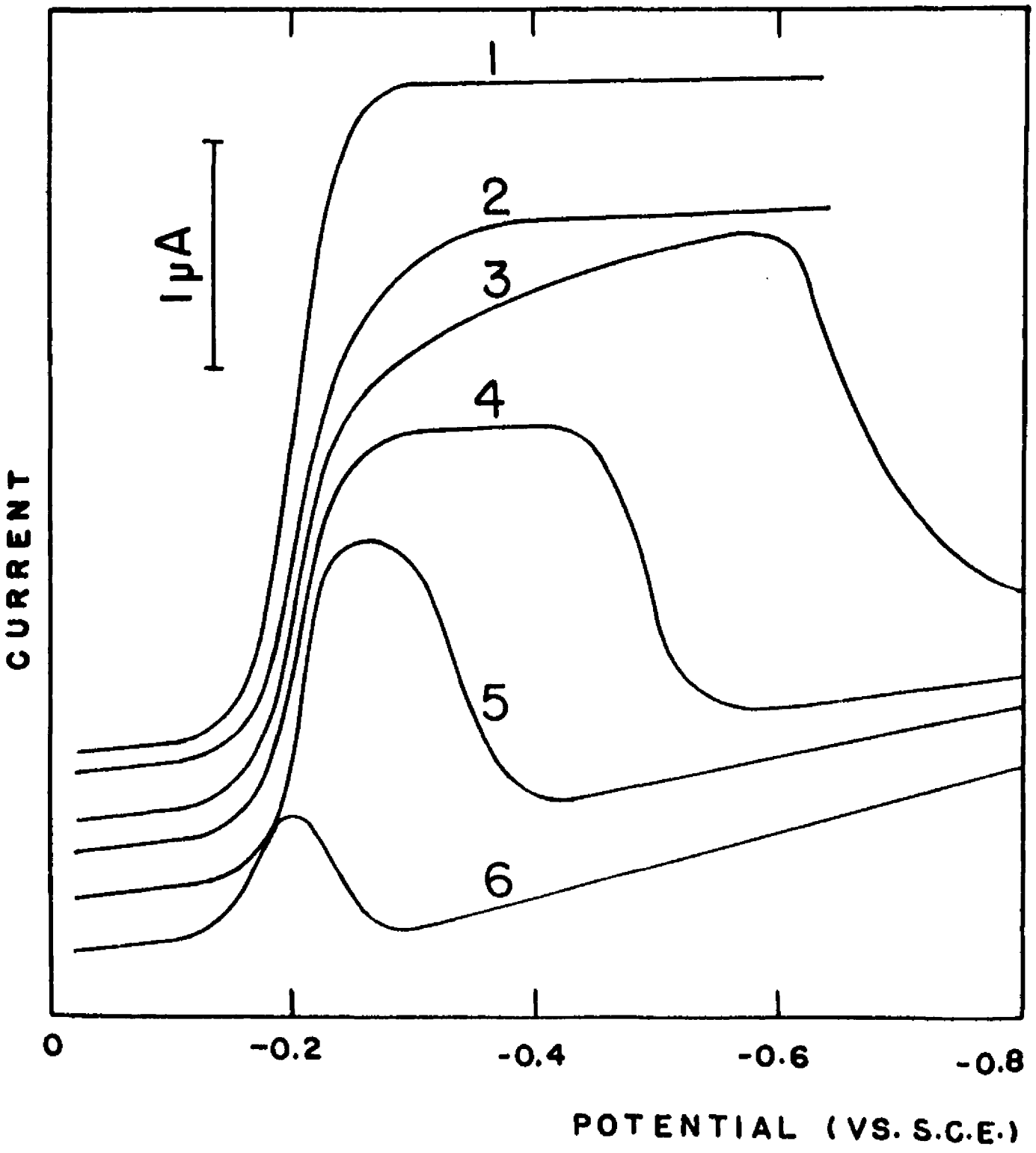

Fig. 9. Polarograms of 1.0 mM Cu(II) in 0.5 M sodium citrate with varying amounts of quinoline. Millimolar concentrations of quinoline: (1) 0; (2) 0.1; (3) 0.5; (4) 1; (5) 2.5; (6) 5. Temperature, 25°.

the supporting electrolyte to 1 M sodium citrate-0.1 M sodium hydroxide (shifts half wave potential more cathodic for the reduction of both copper citrate complex and quinoline), excellent double waves are observed. The first limiting current results from blocking of the electrode by the adsorbed film. The second limiting current is reached when the blocking film is completely desorbed.

Current-time curves during drop life for the system of Fig. 9 are shown in Fig. 10 with the pertaining data in Table III. Three effects will be discussed, namely, the effect of drop time, quinoline concentration, and potential.

Since the area of the mercury drop (sphere) increases with $t^{2/3}$, t being the time during drop life, the rate of drop growth depends on $t^{-1/3}$ and decreases continuously. In the initial stage of the drop life, the drop grows too rapidly to be fully covered and the faradaic current is not too markedly hindered. The drop becomes progressively covered with adsorbate, and the current decreases at the end of the drop life (Fig. 10A). If the drop time is long enough (perhaps 10 sec.), the decrease in current is soon overcompensated by the increase in area, and the current increases again (Fig. 10B).

The rate of adsorption increases with the volume concentration of adsorbate. Hence, the minimum in current-time curves is shifted toward shorter times as the concentration of adsorbate increases (Fig. 10C and 10D). The minimum in current-time curves disappears at large concentrations of adsorbed species.

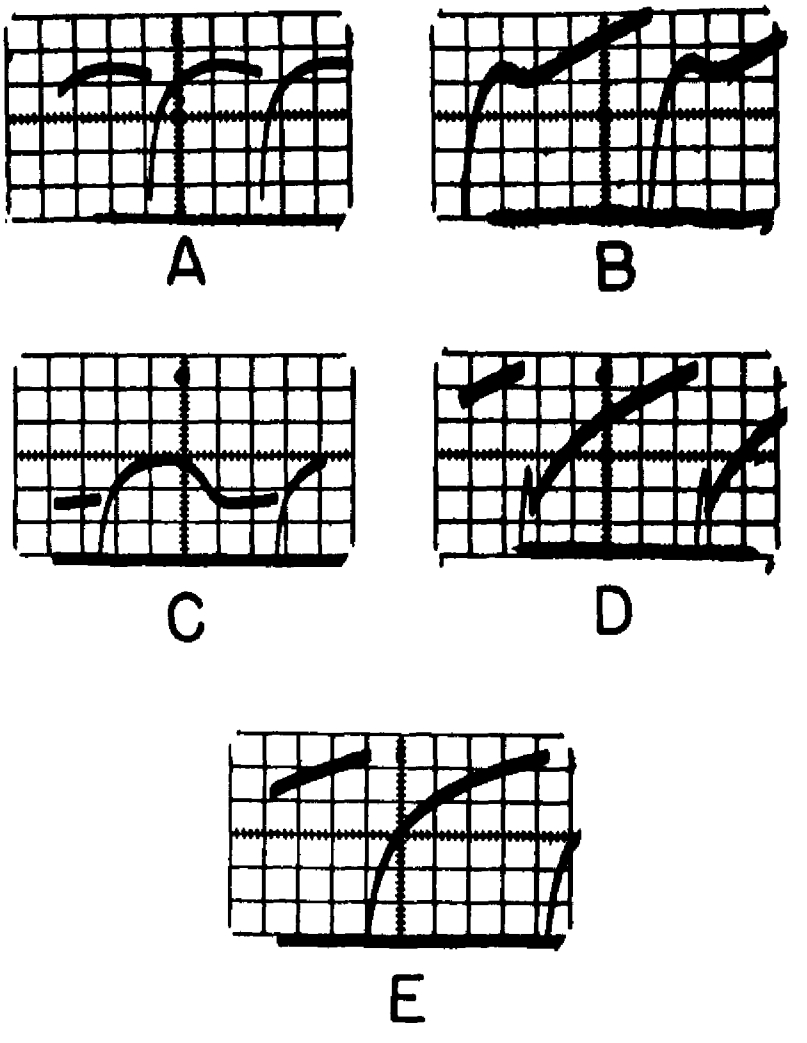

Fig. 10. Current-time curves for 1.0 mM Cu(II) in 0.5 M sodium citrate. See data in Table III.

TABLE III

DATA[a] FOR FIG. 10

Plate	C[b] mM	E volts vs. S.C.E.	H[c] cm.	Abscissa scale[f]	Ordinate scale[g]	R[d,e]
A	0.6	0.588	81	1	1	800
B	0.6	0.588	25	2	1	2000
C	0.3	0.887	25	2	1	1000
D	0.6	0.816	25	2	1	2000
E	0.6	0.415	25	2	1	1500

[a] $m = 2.23$ mg. $sec.^{-1}$ at -0.80 volt (vs. S.C.E.) and for H = 81 cm.

[b] Concentration of quinoline.

[c] Head of mercury.

[d] Resistance (in series with cell) connected to cathode-ray oscilloscope.

[e] Temperature, 25°.

[f] 1 sec./square.

[g] 1 mV/square.

The electrode coverage can be adjusted at will by variation of the potential (2, 10), all other conditions being identical; and the shape of current-time curves changed with potential.[1] If the potential is sufficiently close to one of the two desorption peaks of the differential capacity curve, the coverage is small, and the minimum in the current-time curves disappears (Fig. 10E). Compare plates B, D, and E of Fig. 10 which were obtained under identical conditions except that the potential was changed.

If the limiting current is relatively small in comparison with the diffusion current which would be observed in the absence of adsorbed substance, "blocking" by the film primarily controls the current. There is little concentration polarization for the reducible substance, and the limiting current is essentially proportional to the electrode area. The limiting current then is practically independent of the head of mercury.[2] Conversely, when the limiting current is almost equal to the diffusion current, mass transfer is rate determining, and the limiting current virtually obeys the Ilkovic equation. Under these conditions, the limiting current is essentially proportional to the square root of the head of mercury. The intermediate behavior is more complex and corresponds to current-time curves with a minimum.

---

[1]Another reason is the dependence of current on time for irreversible waves.

[2]The limiting current is proportional to $(mt)^{2/3}$, and m is proportional to H while t is inversely proportional to H, H being the head of mercury corrected for the back pressure.

The foregoing conclusions are borne out experimentally, and it is observed that the relationship between maximum current during drop life and the head of mercury depends on the concentration of adsorbable substance (Fig. 11). Limiting currents of Fig. 11 were measured at the minimum of current-potential curves (see Fig. 9).

Results for a few systems are summarized in Fig. 12 and Table IV. Two effects will be discussed: (a) the influence of the nature of the reduced species for a given adsorbed film (curves A and B), and (b) the effect of the nature of the adsorbed substance for a given reducible species (curves C and D).

Curve A which indicates only a very small effect of adsorption on limiting currents is readily interpreted. The diffusion process is not changed appreciably because the thickness of the diffusion layer is very large in comparison with the average distance between holes in the film.[3] Furthermore, the rate of reduction of cadmium ions is high (the exchange current is large and $E \ll E^{o}$), and consequently partial coverage does not affect much the limiting current (11). Of course, the positions of the holes changes continuously because of the adsorption-desorption process; but this does not affect the argument.

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[3] A uniform distribution of the adsorbed species is assumed.

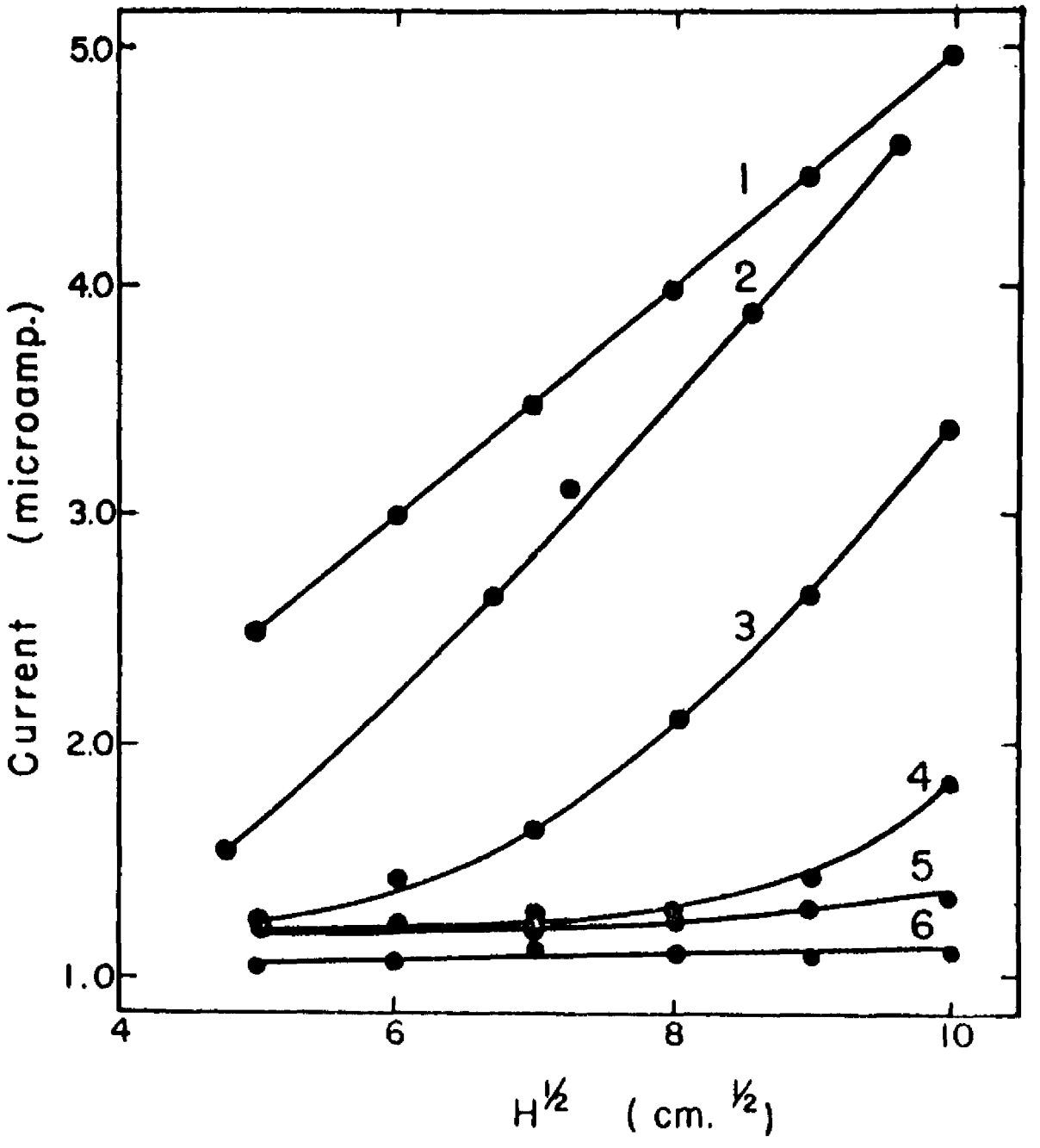

Fig. 11. Limiting current at 25° against head of mercury for the reduction of 1.0 mM Cu(II) in 0.5 M sodium citrate in presence of quinoline. Millimolar concentrations of quinoline: curve (1), 0; (2) 0.3; (3) 0.4; (4) 0.6; (5) 1; (6) 3.

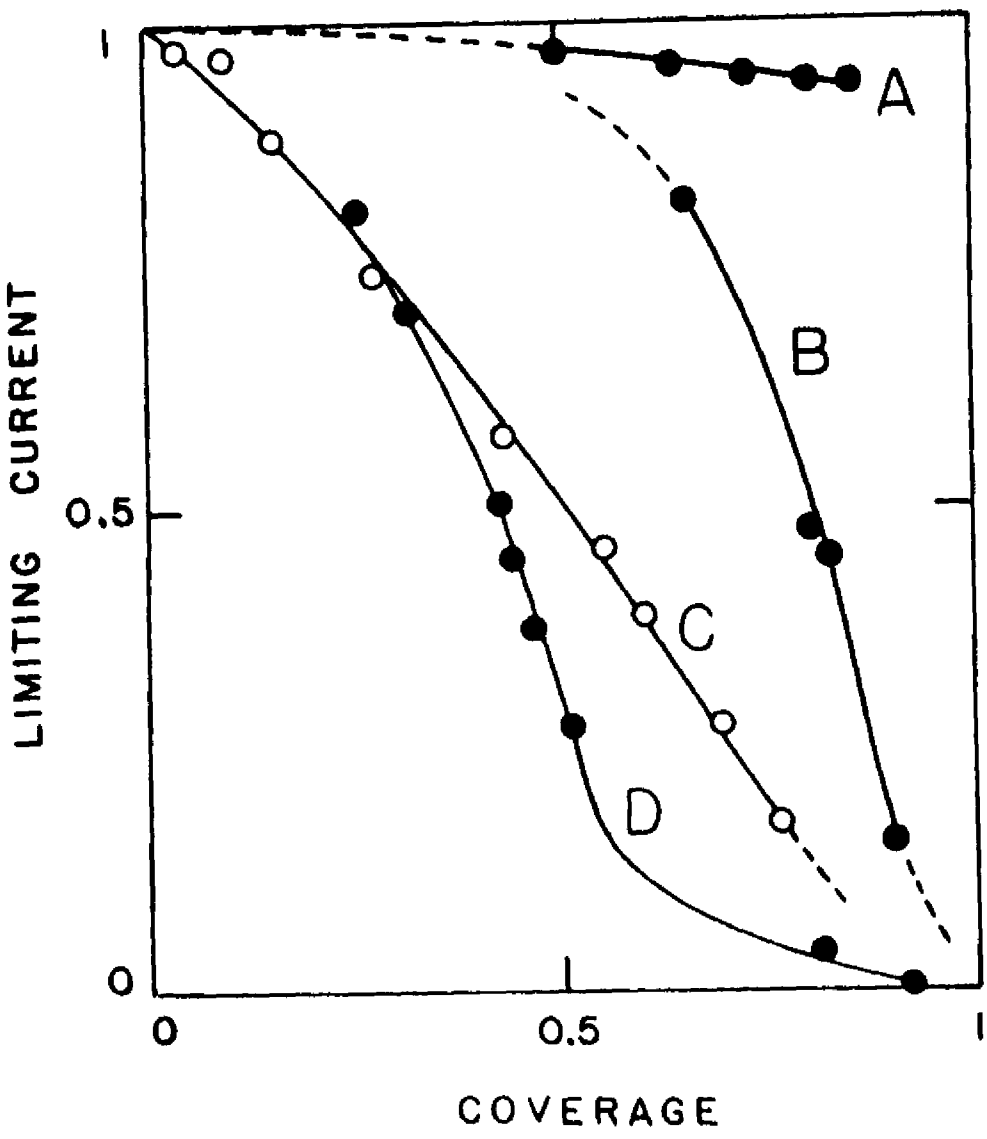

Fig. 12. Variations of limiting current at the end of drop life with coverage. Currents expressed as the fraction of the diffusion current observed without adsorbed substance. A, 2.0×10^{-3} M Cd^{++} in 1 M potassium chloride plus thymol; B, 2.0×10^{-3} M Cd^{++} in 0.5 M sodium citrate plus thymol; C, 4.0×10^{-3} M Cu^{++} in 1 M sodium citrate and 0.1 M sodium hydroxide plus n-hexyl alcohol; D, same as C except quinoline instead of n-hexyl alcohol. Potentials at which currents were measured: -0.72 (A and B) and -0.70 (C and D) volt vs. S.C.E.

Table IV

Electrode Coverage at the End of the Drop Life[a]

n-Hexyl Alcohol		Quinoline		Thymol		
mM	θ^c	mM	θ^d	mM	θ^d	θ^e
0.12	0.039	0.039	0.25	0.15	0.50	0.66
.23	.089	.058	.32	.22	.65	.80
.34	.15	.077	.38	.30	.73	.83
.45	.27	.11	.42	.36	.81	---
.54	.44	.15	.44	.49	.86	.90
.64	.55	.18	.45			
.74	.60	.25	.51			
.94	.69	.30	.80			
1.26	.76	.63	.92			

[a] Temperature 30°C.

[b] Capillary characteristics: m = 2.70 mg. $sec.^{-1}$, t = 3.5 sec.

[c] 1.0 M sodium citrate, 0.1 M sodium hydroxide, -.70 volt (vs. S.C.E.)

[d] 1.0 M potassium chloride, -.72 volts (vs. S.C.E.)

[e] 0.5 M sodium citrate, -.72 volts (vs. S.C.E.)

The above analysis is also applicable to curve B, but the relative bulkiness of the cadmium citrate complex causes the current to decrease markedly for $\theta > 0.5$. The decrease in current is not observed with cadmium chloride (curve A) because of the smaller ionic size. This effect of the ionic size was confirmed for other cases: The limiting current for the reduction of thallous ion, which is small (high diffusion coefficient in comparison with other ions) did not decrease upon the addition of n-hexyl alcohol (0.01M) or quinoline (0.005 M). Likewise, thymol (0.005M) had little effect on the limiting current for the reduction of cadmium in 1 M chloride. No effect was observed for cupric ion in nitrate medium upon the addition of n-hexyl alcohol (0.01 M); whereas this substance (0.001 M) completely suppressed the wave in sodium citrate-sodium hydroxide medium.

Further confirmation of the effect of ionic size was obtained from the current time curves during drop life (Fig. 13). Thus, at the beginning of the drop life, the drop grows very rapidly, the coverage is relatively small (see also Fig. 10), and the current increases rapidly. However, the rate of growth decreases continuously, and the coverage increases, thus causing a drop in current. Further growth of the drop causes the current to increase. It is seen from Fig. 13 that the addition of thymol hardly affects the current-time curves for the reduction of cadmium ion in chloride medium; whereas the characteristic maxima are observed in the citrate medium. This difference results from the difference in ionic size and not from the rather small

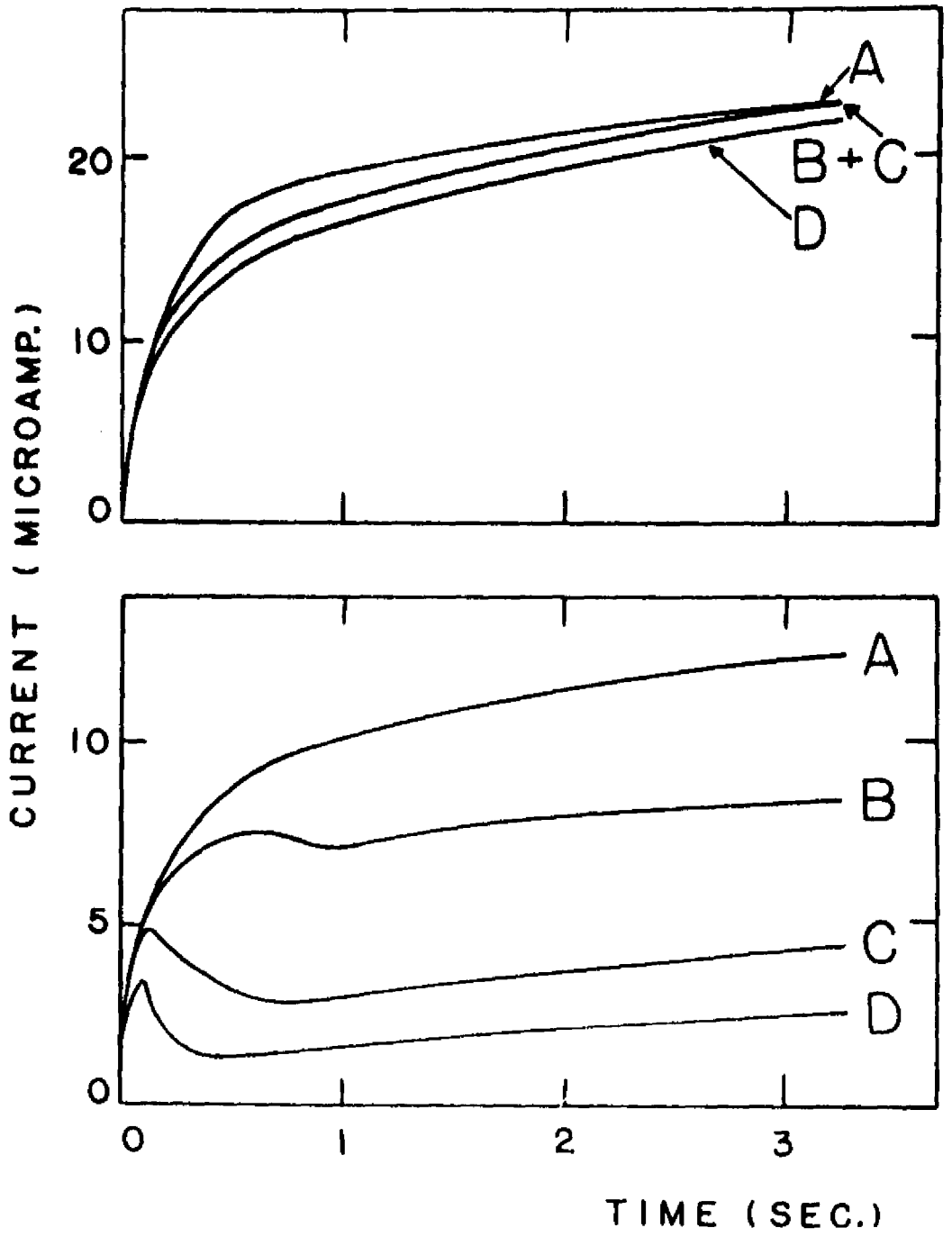

Fig. 13. Current-time curves during drop life for 2.0 mM Cd^{++} in 1 M potassium chloride (top) and 0.5 M sodium citrate (bottom) for a varying concentration of thymol. Thymol concentration in mM: A(0), B(0.22), C(0.36), and D(0.49). (Curves were obtained from oscillographic traces.)

variation in coverage from one medium to the other (Table IV).

The effect of the nature of the adsorbed substance for a given reducible species is apparent from the curves C and D in Fig. 12. This difference is undoubtedly related to the film structure and the average "size" of the holes in the film.

Analytical application could be made by proper combination of these two effects (size reducible species and structure of adsorbed film), and it should be possible in some cases to resolve waves, which in the absence of adsorbed species, are observed in the same range of potentials.

Implications with Respect to Analysis of Waves.

Even when adsorption of a foreign substance has little effect on the limiting current, the overvoltage for polarographic waves is increased and current-potential curves become more irreversible (Fig. 14). An approximate analysis of these waves can be made by the method of Koutecky (25, 26) provided that two conditions are fulfilled: (a) the equilibrium surface concentration of the adsorbed species is practically independent of potential over the range of potentials being investigated; (b) the bulk concentration of adsorbed species is so large that adsorption equilibrium is essentially reached during the entire drop life. These conditions often are not fulfilled and the interpretation of irreversible waves for contaminated solutions is open to question. It is obvious that conditions yielding a current-time curve with a maximum (Fig. 13 bottom) do not correspond to the conditions of mass transfer of the reducible

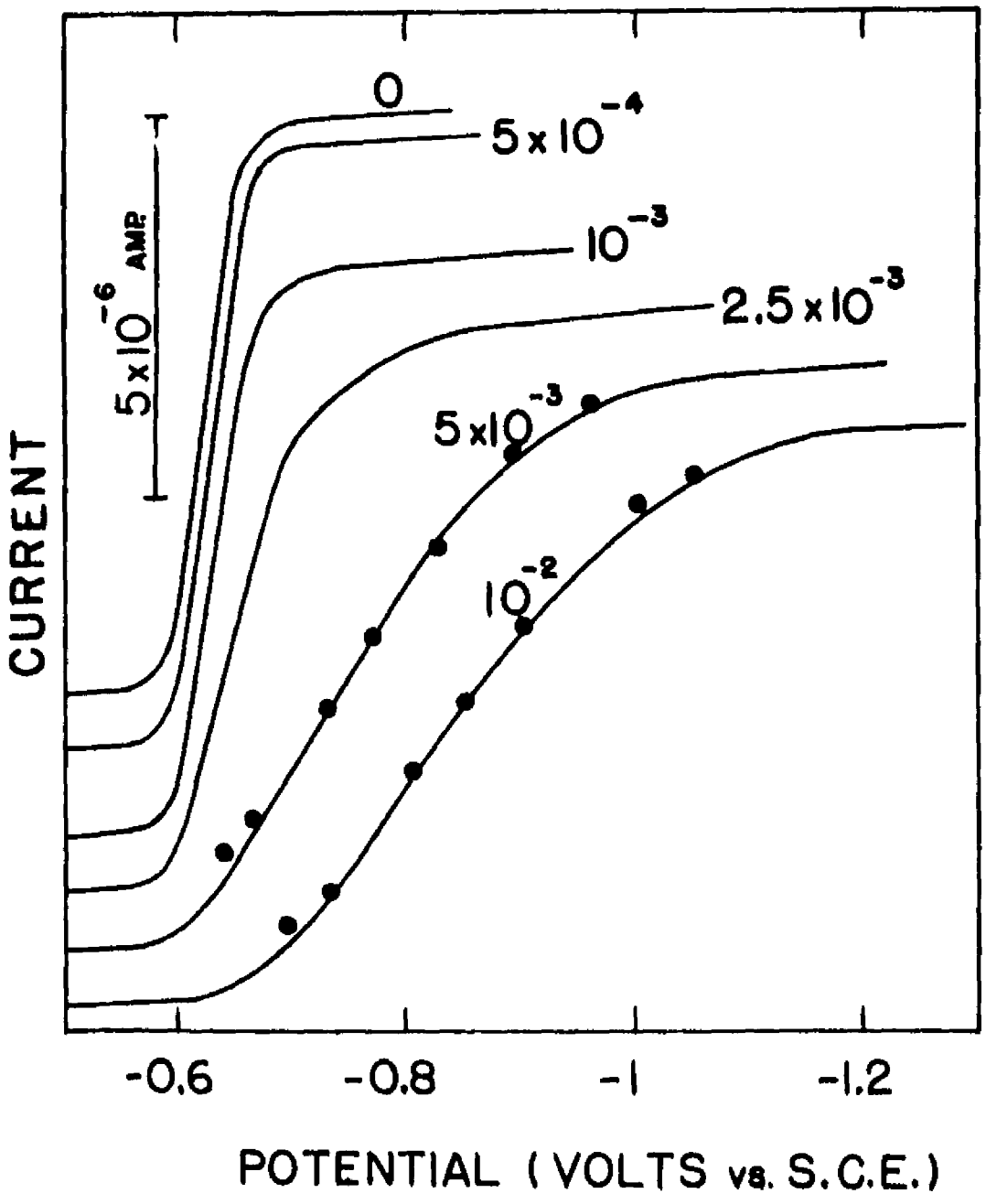

Fig. 14. Polarographic waves for 1.0 mM Cd^{++} in 1 M sodium sulfate with varying concentrations of n-hexyl alcohol (numbers on each curve in M). Maximum current during drop life is plotted. m = 2.25 mg./sec., t = 3.68 sec.

and reduced species which are assumed in the absence of adsorption. It is seen in Fig. 14 that experimental currents and calculated ones agree quite well for reasonable kinetic data for the two highest concentrations of n-hexyl alcohol. No agreement could be obtained for lower concentrations of n-hexyl alcohol, and discrepancies on the current in the ascending branch of these waves were as large as 30 - 100 per cent. Kinetic data used in these calculations were as follows: values of apparent k_s (no correction for coverage), 1 and 2.2 x 10^{-4} cm. $sec.^{-1}$ for the 10 and 5 x 10^{-3} M n-hexyl alcohol solutions, respectively; α = 0.15 and 0.17, respectively.

CHAPTER VI

CONCLUSION

Three novel ideas were developed in this investigation: (a) adsorption with diffusion control is a slow process; (b) it is possible by coverage measurements to determine the variations in kinetic parameters for electrode processes with electrode coverage; (c) the blocking of electrode reactions by adsorption of foreign substances (not reduced or oxidized) can be studied as a function of electrode coverage. A variety of observations which had remained unexplained in the literature were interpreted on a rational basis (overvoltage phenomena, electrode contamination, current-time and current-potential curves in polarography, time dependence in surface tension measurements, etc.), and new modes of approach for further study of the effects of adsorption on electrode processes have been developed.

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Isaac Trachtenberg was born in New Orleans, Louisiana, on August 20, 1929. He attended public shools in New Orleans and Galveston, Texas, and he graduated from Ball High School in Galveston in June, 1946. The following fall he entered Rice Institute, Houston, where he was awarded a Bachelor of Arts degree after four years of study. He then entered graduate school at Louisiana State University and, working with Dr. G. L. Eichhorn, he received a Master of Science degree in August, 1952. In April, 1953, he was inducted into the armed services and served with the Chemical Corps until January, 1955. Upon leaving the army, he re-entered Louisiana State University where is now a candidate for the degree of Doctor of Philosophy.

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Major Field: Chemistry

Title of Thesis: Adsorption Kinetics and Electrode Processes

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination: May 2, 1957